

# Non-equilibrium thermodynamics. IV: Generalization of Maxwell, Claussius-Clapeyron and Response Functions Relations, and the Prigogine-Defay Ratio for Systems in Internal Equilibrium\*

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(December 15, 2010)

## Abstract

We follow the consequences of internal equilibrium in non-equilibrium systems that has been introduced recently [Phys. Rev. E **81**, 051130 (2010)] to obtain the generalization of Maxwell's relation and the Clausius-Clapeyron relation that are normally given for equilibrium systems. The use of Jacobians allow for a more compact way to address the generalized Maxwell relations; the latter are available for any number of internal variables. The Clausius-Clapeyron relation in the subspace of observables show not only the non-equilibrium modification but also the modification due to internal variables that play a dominant role in glasses. Real systems do not directly turn into glasses (GL) that are frozen structures from the supercooled liquid state L; there is an intermediate state (gL) where the internal variables are not frozen. Thus, there is no single glass transition. A system possess several kinds of glass transitions, some conventional ( $L \rightarrow gL$ ;  $gL \rightarrow GL$ ) in which the state change continuously and the transition mimics a *continuous* or second order transition, and some apparent ( $L \rightarrow gL$ ;  $L \rightarrow GL$ ) in which the free energies are discontinuous so that the transition appears as a *zeroth order* transition, as discussed in the text. We evaluate the Prigogine-Defay ratio  $\Pi$  in the subspace of the observables at these transitions. We find that it is normally different from 1, except at the conventional transition  $L \rightarrow gL$ , where  $\Pi = 1$  regardless of the number of internal variables.

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## I. INTRODUCTION

### A. Previous Results

In a series of papers, we have begun to develop non-equilibrium thermodynamics starting from the second law and ensuring the additivity of entropy as a state function [1–3]. The central idea in this approach is that of *internal equilibrium* within a macroscopic system  $\Sigma$  surrounded by an extremely large medium  $\tilde{\Sigma}$ ; the two form an isolated system  $\Sigma_0$  as shown in Fig. 1. While the entropy  $S(t)$  and the general non-equilibrium thermodynamic potential  $\Omega(t)$ , see [2] for more details, such as the non-equilibrium Gibbs free energy  $G(t)$  of the system *exist* even when the system is not in internal equilibrium, the Gibbs fundamental relation exists only when the system is in internal equilibrium:

$$dS(t) = \mathbf{y}(t) \cdot d\mathbf{X}(t) + \mathbf{a}(t) \cdot d\mathbf{I}(t), \quad (1)$$

where  $\mathbf{X}(t)$  and  $\mathbf{I}(t)$  represent the set of observables and the set of internal variables, respectively, to be collectively denote by  $\mathbf{Z}(t)$ . The entropy  $S(\mathbf{Z}(t), t)$  away from equilibrium, no matter how far from equilibrium, is normally a function of  $\mathbf{Z}(t)$  and  $t$ . However, when the system is in internal equilibrium, where Eq. (1) remains valid,  $S(t)$  has *no* explicit  $t$ -dependedence; the temporal evolution of the entropy in this case comes from the time-dependence in  $\mathbf{Z}(t)$ , with  $\mathbf{X}(t)$  and  $\mathbf{I}(t)$  still independent of each other. The coefficient  $\mathbf{y}(t)$  and  $\mathbf{a}(t)$  represent the derivatives of the entropy and are normally called the internal field and the internal affinity, respectively. The energy  $E$ , volume  $V$  and the number of particles  $N$  play a very special role among the observables, and the corresponding internal fields are given by

$$\frac{1}{T(t)} = \left( \frac{\partial S(t)}{\partial E(t)} \right)_{\mathbf{Z}'(t)}, \quad \frac{P(t)}{T(t)} = \left( \frac{\partial S(t)}{\partial V(t)} \right)_{\mathbf{Z}'(t)}, \quad \frac{\mu(t)}{T(t)} = - \left( \frac{\partial S(t)}{\partial N(t)} \right), \quad (2)$$

where  $\mathbf{Z}'(t)$  denotes all other elements of  $\mathbf{Z}(t)$  except the one used in the derivative. Thus, internal temperature, pressure, etc. have a meaning only when the system comes into internal equilibrium. In general, the internal field  $\mathbf{y}(t)$  and affinity  $\mathbf{a}(t)$  are given by

$$\mathbf{y}(t) \equiv \frac{\mathbf{Y}(t)}{T(t)} \equiv \left( \frac{\partial S(t)}{\partial \mathbf{X}(t)} \right)_{\mathbf{Z}'(t)}, \quad \mathbf{a}(t) \equiv \frac{\mathbf{A}(t)}{T(t)} \equiv \left( \frac{\partial S(t)}{\partial \mathbf{I}(t)} \right)_{\mathbf{Z}'(t)}. \quad (3)$$

The fields of the medium  $T_0, P_0, \mu_0$ , etc., which we collectively denote by  $\mathbf{Y}_0$ , are different from the internal fields of the system unless the latter comes to equilibrium with the medium.

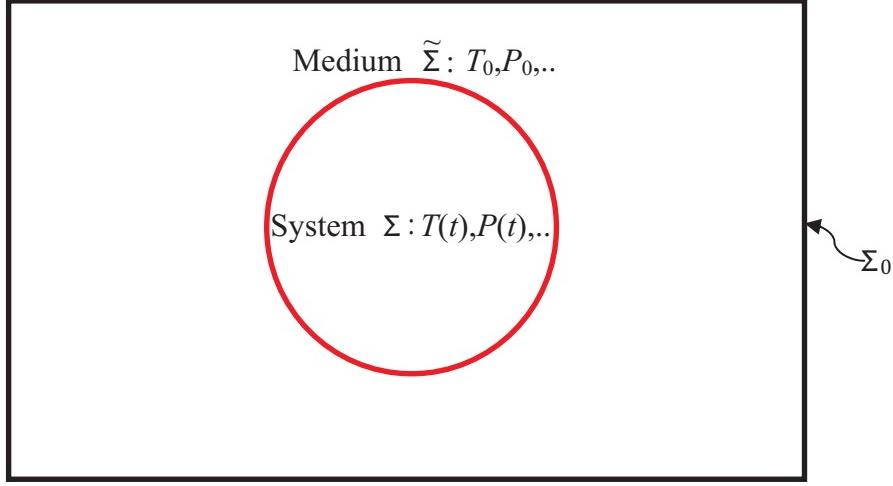


FIG. 1: Schematic representation of a system  $\Sigma$  and the medium  $\tilde{\Sigma}$  surrounding it to form an isolated system  $\Sigma_0$ . The medium is described by its fields  $T_0, P_0$ , etc. while the system, if in internal equilibrium (see text) is characterized by  $T(t), P(t)$ , etc.

The same is also true of the affinity, except that the affinity vector  $\mathbf{A}_0 = 0$  for the medium; see II.

From now on, we will only consider the case when the system is in internal equilibrium. The heat transfer is given by

$$dQ = T(t)dS(t) = T_0 d_e S(t), \quad (4)$$

where  $d_e S(t)$  is the entropy exchange with the medium. The irreversible entropy generation  $d_i S(t)$  within the system is given by

$$d_i S(t) \equiv dS(t) - d_e S(t) \geq 0.$$

Thus, as long as the system is not in equilibrium,  $T(t) \neq T_0$ ; accordingly,  $d_i S(t) > 0$  in accordance with the second law. There is irreversible entropy production even when the system is in internal equilibrium; the latter only allows us to introduce the internal fields and affinities via Eqs. (2) and (3).

In the absence of any internal variables, the Gibbs fundamental relation is given by

$$T(t)dS(t) = dE(t) + P(t)dV(t) - \mu(t)dN(t) \quad (5)$$

for the special case when  $\mathbf{X}(t)$  only contains  $E(t), V(t)$  and  $N(t)$ . For a fixed number of particles, the last term would be absent. As said above, the temperature, pressure, etc.

of the medium and the system are usually different when the system is out of equilibrium with the medium. Only in equilibrium do they become equal, in which case, the Gibbs fundamental relation in Eq. (5) reduces to the standard form

$$T_0 dS_{\text{eq}} = dE_{\text{eq}} + P_0 dV_{\text{eq}} - \mu_0 dN_{\text{eq}}, \quad (6)$$

in which none of the quantities has any time-dependence; the extensive quantities represent the equilibrium values and are denoted by the additional suffix. One normally considers a system with fixed number of particles, in which case, the last term is absent in Eq. (6). In the following, we will not explicitly show the additional suffix unless clarity is needed. The following Maxwell relations that follow from the Gibbs fundamental relation, see Eq. (6), are well-known and can be found in any good text-book such as [4] on thermodynamics:

$$\begin{aligned} \left( \frac{\partial T_0}{\partial V} \right)_{S,N} &= - \left( \frac{\partial P_0}{\partial S} \right)_{V,N}, & \left( \frac{\partial T_0}{\partial P_0} \right)_{S,N} &= \left( \frac{\partial V}{\partial S} \right)_{P_0,N}, \\ \left( \frac{\partial P_0}{\partial T_0} \right)_{V,N} &= \left( \frac{\partial S}{\partial V} \right)_{T_0,N}, & \left( \frac{\partial S}{\partial P_0} \right)_{T_0,N} &= - \left( \frac{\partial V}{\partial T_0} \right)_{P_0,N}. \end{aligned} \quad (7)$$

In equilibrium, there is no explicit  $t$ -dependence in  $\mathbf{Z}$ ; moreover, the internal variable  $\mathbf{I}$  is no longer independent of  $\mathbf{X}$ . The equilibrium field and affinity of the system become equal to those of the medium ( $\mathbf{Y}_0$  and  $\mathbf{A}_0 = 0$ ); see [2]. Thus, the Gibbs fundamental relation reduces to

$$dS = \mathbf{y}_0 \cdot d\mathbf{X}, \quad (8)$$

compare with Eq. (6). The equilibrium value of the internal variable can be expressed as a function of the equilibrium value of  $\mathbf{X}$ :

$$\mathbf{I} = \mathbf{I}_{\text{eq}}(\mathbf{X}_{\text{eq}}).$$

We now observe the similarity between the Gibbs fundamental relations in Eqs. (6) and (8). This strongly suggests that there may also exist analogs of the Maxwell relations or other important relations that are based on Eq. (8) for a system that, although not in equilibrium with the medium, is in internal equilibrium. In this sequel to the earlier papers [1–3], which we denote by I, II, and III, respectively, we develop the consequence of this internal equilibrium thermodynamics for important relations such as Maxwell relations, Clausius–Clayperon equation, etc. These extensions will play an important role in non-equilibrium systems that are nonetheless in internal equilibrium.

The time-variation of the internal temperature  $T$  of a non-equilibrium system such as a glass is due to the time dependence of the observable  $\mathbf{X}(t)$  such as  $E(t), V(t)$ , etc. and of the internal variable  $\mathbf{I}(t)$ . For example, at fixed  $T_0$ , the internal temperature will continue to change during structural relaxation. The internal temperature will also change if the temperature of the medium changes. Thus

$$dT = \left( \frac{\partial T}{\partial \mathbf{X}} \right) \cdot d\mathbf{X} + \left( \frac{\partial T}{\partial \mathbf{I}} \right) \cdot d\mathbf{I}.$$

The rate of change of the internal temperature can be expressed in terms of the rate of change  $r = dT_0/dt$ :

$$\frac{dT}{dt} = \left( \frac{\partial T}{\partial \mathbf{X}} \right) \cdot \frac{d\mathbf{X}}{dt} + \left( \frac{\partial T}{\partial \mathbf{I}} \right) \cdot \frac{d\mathbf{I}}{dt}. \quad (9)$$

Similarly,

$$\frac{dT}{dT_0} = \left( \frac{\partial T}{\partial \mathbf{X}} \right) \cdot \frac{d\mathbf{X}}{dT_0} + \left( \frac{\partial T}{\partial \mathbf{I}} \right) \cdot \frac{d\mathbf{I}}{dT_0}. \quad (10)$$

The same analysis can be carried out for other internal fields.

## B. Present Goal

Our aim in this work is to follow the consequences of internal equilibrium in a non-equilibrium system to find the generalization of Maxwell's relations, the Clausius-Clapeyron relation, and the relations between response functions to non-equilibrium states. We will be also be interested in glasses in this work; they are traditionally treated as non-equilibrium states. Therefore, we begin with a discussion of what is customarily called a glass and the associated glass transition in Sect. II. A careful discussion shows that the term does not refer to one single transition; rather, it can refer to different kinds of transitions, some of which appear similar to the conventional transitions in equilibrium, but the other refer to apparent transitions where the Gibbs free energy cannot be continuous. There are some well-known approximate approaches to glasses. We will briefly discuss them. We then turn to our main goal to extend the Maxwell's relations, where Jacobians are found to be quite useful. Therefore, we introduce Jacobians and their various important properties in Sect. III A. This is technical section, but we provide most of the required details so that the clarity of presentation is not compromised. An important part of this section is to show that the Jacobians can be manipulated in a straight forward manner even in a subspace of the variables. This is important as the observations require manipulating the observables and

not the internal variables. Thus, the experimental space refers to a subspace (Sect. III B) of the space where non-equilibrium thermodynamics is developed. Thermodynamic potentials for non-equilibrium states are formulated in Sect. IV. We develop the generalization of the Maxwell's relations in Sect. V. We discuss generalization of the Clausius-Clapeyron relation in Sect. VI, where we also discuss the conditions for phase transitions in non-equilibrium states. The response functions such as the heat capacities, compressibilities and the expansion coefficients and various relations among them are developed for non-equilibrium states in Sect. VII. The Prigogine-Defay ratio for glasses are evaluated at various possible glass transitions in Sect. VIII. We compare our approach with some of the existing approaches in determining the ratio in this section. The last section contains a brief summary of our results.

## II. GLASS TRANSITIONS AND APPARENT GLASS TRANSITIONS

An example of non-equilibrium systems under investigation here is a glass [5]; see Figs. 2 and 3. A supercooled liquid L is a *stationary* (time-independent) metastable state [5], which for our purpose, represents an equilibrium state (by not allowing the crystalline state into consideration), and is shown by the curve ABF under isobaric condition at a fixed pressure  $P_0$  of the medium. We will refer to the equilibrium liquid always as L in the following. In contrast, a non-equilibrium liquid state will be designated gL here, and represents a *time-dependent* metastable state [5]. The choice of gL is to remind us that it is a precursor to the eventual glass GL at a lower temperature. The equilibrium liquid L is obtained by cooling the liquid L and waiting long enough at each for it to come to equilibrium with the medium. However, if it is obtained at a fixed cooling rate  $r$ , then at some temperature  $T_{0g}(P_0)$ , L cannot come to equilibrium and turns into gL; the resulting curve BD leaves ABF tangentially at B, and gradually turns into an isobaric glass GL represented by the segment DE at D, when the viscosity becomes so large ( $\sim 10^{13}$  poises) that it appears as a solid. At B, the transition is from an equilibrium liquid L to a non-equilibrium liquid form gL, and will be called the L-gL transition. In the literature, it is commonly known as a transition from an ergodic state (L) to a non-ergodic state (gL). In our opinion, this is a misnomer, as the concept of *ergodicity* refers to the long-time, indeed the infinite-time, behavior. In this limit, there will be no gL, only L. Therefore, we will refer to this transition at  $T = T_{0g}(P_0)$ .

as a L-gL transition or a *precursory* glass transition. The true glass transition at D is not a transition from L to GL, but a transition from gL to GL. We will refer to the glass transition at the lower temperature  $T_{0G}(P_0)$  at D as the *actual* glass transition, or simply the glass transition. The transition region BD represents a time-dependent metastable supercooled liquid (to be distinguished from the stationary metastable supercooled liquid L denoted by ABF), which turns into a glass at D. The expansion coefficient in the glass is almost identical to that of the corresponding crystal below D. The glass continuously emerges out of gL at D, whose location is also determined by the rate  $r$  of cooling. The relaxation time  $\tau$  of the system (the supercooled liquid) becomes equal (really comparable) to the observation time  $\tau_{\text{obs}}$  at B. As seen in Fig. 2, the volume remains continuous at B and D at the two glass transitions. The same is also true of the entropy. Indeed, the state of the system changes continuously at B and D, which is highly reproducible for a given cooling rate  $r$  or the observation time  $\tau_{\text{obs}}$ . Thus, the points B and D can be taken as a well-defined and unique glass transition temperatures  $T_{0g}(P_0)$  and  $T_{0G}(P_0)$  associated with the point B and D, respectively, in both figures. Both transitions represent a non-equilibrium version of a continuous transition (See Sect. VI for elaboration on this point), where not only the Gibbs free energy, see Fig. 3, but also its derivatives are continuous. The non-equilibrium nature of the transition appears in the dependence of the value of  $T_{0g}(P_0)$  and  $T_{0G}(P_0)$  on the rate of cooling. The continuity of the Gibbs free energy at B and D makes them as genuine candidates as (glass) transition points, a requirement of a transition in equilibrium thermodynamics. Therefore, both these transitions will be collectively called *conventional transitions* in this work.

Unfortunately, the idea of a glass transition was formulated as a transition between L and GL. Thus, neither of the above two glass transitions represent the glass transition in the original sense. As the glass is considered a frozen state, it is common to assume that over the region DE, the glass has its internal variables denoted by **I** frozen at its value  $\mathbf{I}_G$  at D, even though its observables denoted by **X** continue to change. On the other hand, the internal variables and the observables continue to change over BD from their values at B to their values at D. Consequently, the properties such as the volume of gL, which is shown schematically in Fig. 2, gradually change to those of the glass at lower temperatures. Thus, the glass transition from AB to DE is not a sharp transition. It can be argued, as we have done above, that B and D should be taken as the glass transition points. However, the

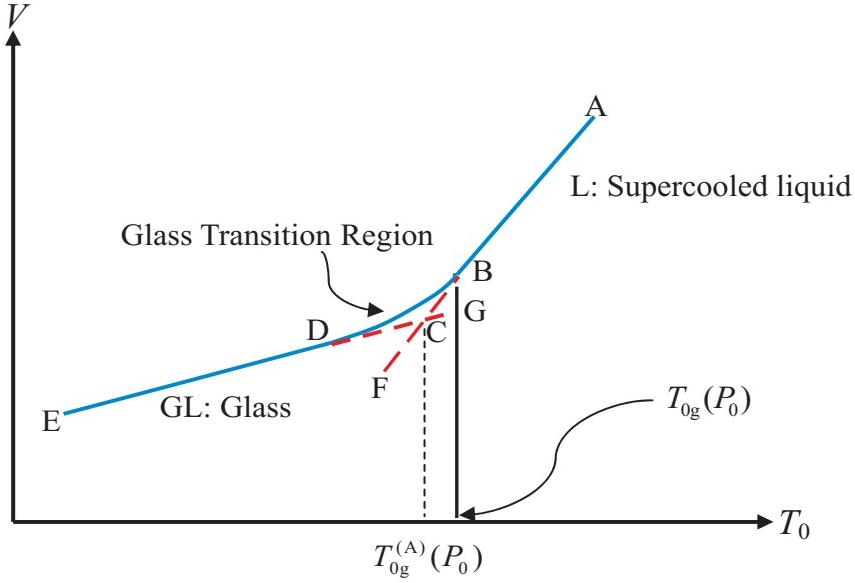


FIG. 2: Schematic form of isobaric  $V$  as a function of  $T_0$  for a given cooling rate. The pressure is fixed at  $P_0$ . The supercooled liquid turns gradually into a glass through the glass transition region. The transition temperature  $T_{0g}(P_0)$  is identified as the temperature at B, where the actual volume begins to deviate from the extrapolated supercooled liquid volume BC. On the other hand, the apparent glass transition temperature  $T_{0g}^{(A)}(P_0)$  is the temperature where the extrapolated glass volume DC meets the extrapolated supercooled liquid volume BC as indicated in the figure; this temperature lies in the glass transition region.

practice in the field is to take a point between BD as a transition point obtained by electing some well-defined rule of selection; see for example [6] for a good discussion of various ways of identifying the glass transition temperature. One such rule commonly used is to consider the volume of the system and introduce an *apparent* glass transition temperature  $T_{0g}^{(A)}(P_0)$  by the *equilibrium continuation* of the volume BCF of AB and by the *extrapolation* of the volume DCG of DE to find their crossing point C. The state of the glass following Tool and Narayanaswamy [7, 8] is then *customarily* identified by the point C on DC. However, there is no reason to take the state at C to represent any real glass, as the extrapolation does not have to satisfy non-equilibrium thermodynamics; the latter is valid only along the physical path DB for the *given history* of preparation such as determined by the fixed rate  $r$  of cooling during vitrification. The glass at  $T_{0g}^{(A)}(P_0)$  must be described by the point on

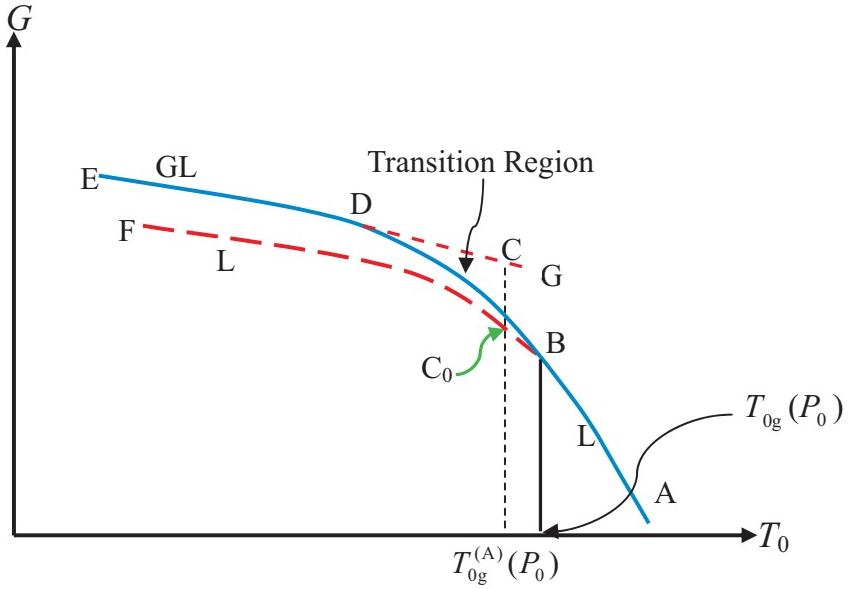


FIG. 3: Schematic form of the isobaric Gibbs free energy  $G$  shown by the continuous curve ABDE as a function of the medium temperature  $T_0$  at a fixed pressure  $P_0$ . The extrapolation of the glassy portion (GL) along DCG and the supercooled liquid (L) portion ABC<sub>0</sub>F do not meet; the glassy Gibbs free energy at point the apparent glass transition C, where  $T_0 = T_{0g}^{(A)}(P_0)$ , is higher than that at C<sub>0</sub> on the continuous curve L at the same temperature  $T_{0g}^{(A)}(P_0)$ , showing that the extrapolation results in a more unstable state at the apparent glass transition C than the physical state C<sub>0</sub> on the continuous curve. The Gibbs free energies match at the glass transition temperature  $T_{0g}(P_0)$  at B.

DB corresponding to  $T_{0g}^{(A)}(P_0)$  if we wish to employ non-equilibrium thermodynamics. To be sure, one can find a slow enough cooling rate than the one used to obtain gL at B so that the point B actually coincides with the point C on ABF, as the latter represents L. However, the gL that will emerge at C for the slower cooling rate has nothing to do with the extrapolated state C on DCG. Because of the continuity of the state, the gL at the slower rate at C will have its  $A = 0$  and  $\xi = \xi_{\text{eq}}$  and will have its Gibbs free energy continuous. Moreover, the new gL will follow a curve that will be strictly below BDE. These aspects make the new gL different from the extrapolated GL at C. Taking the point C on CD to represent the glass will be an approximation, which we will avoid in this work, as our interest

is to apply thermodynamics in the study of glasses. Therefore, we will use the extrapolation to only determine  $T_{0g}^{(A)}(P_0)$ , but the real glass and the real liquid states are determined by the curve BD and BCF, respectively, where our non-equilibrium thermodynamics should be applicable.

The location of this temperature  $T_{0g}^{(A)}(P_0)$  depends on the property being extrapolated. We can use the entropy of the system to locate the apparent glass transition temperature, which would invariably give a different value for the apparent glass transition temperature. To call one of these temperatures as a transition temperature is a misnomer for another reason. None of these temperatures represent a "non-equilibrium" thermodynamic transition for the simple reason that the two branches DCG and BCF do not have a common Gibbs free energy at  $T_{0g}^{(A)}(P_0)$  as is clearly seen in Fig. 3. The branch ABC<sub>0</sub>F represents the Gibbs free energy of the equilibrium supercooled liquid, while the segment DE represents the Gibbs free energy of the glass, with the segment BD denoting the Gibbs free energy of the system during the transition region. The extrapolation DCG in Fig. 2 to determine the glass transition temperature  $T_{0g}^{(A)}(P_0)$  corresponds to the extrapolated segment DCG in Fig. 3. The Gibbs free energy of the glass in this extrapolation is given by the point C, while the Gibbs free energy of the supercooled liquid is determined by the point C<sub>0</sub>. Evidently, the two free energies are very different, with that of the glass higher than that of the supercooled liquid, as expected from the non-equilibrium nature of the glassy state.

The above discussion of the apparent glass transition also applies to comparing the glass at D with the corresponding L at  $T_{0G}(P_0)$ , which will represent yet another apparent glass transition temperature. This apparent glass transition has the same problem regarding the Gibbs free energy as the previous one at  $T_{0g}^{(A)}(P_0)$ . However, this transition differs from the apparent glass transition at  $T_{0g}^{(A)}(P_0)$  in that the "glass" at  $T_{0g}^{(A)}(P_0)$  is not a frozen state, while the glass at D is a "frozen" glass to some extent (as it also undergoes structural relaxation in time). It should also be remarked that whether we consider the apparent glass transition at  $T_{0G}(P_0)$  or  $T_{0g}^{(A)}(P_0)$ , the transition is an example of a discontinuity in the Gibbs free energy of the two states. This is different from the precursory glass transition and the actual glass transition at B and D, respectively, where the Gibbs free energy is continuous. Because of the discontinuity in the Gibbs free energies in the apparent glass transitions at  $T_{0G}(P_0)$  and  $T_{0g}^{(A)}(P_0)$ , we will refer to these transitions as *apparent transitions* in this work. Indeed, one can think of these transitions as an analog of a *zeroth order* transition

because of the discontinuity in the Gibbs free energy. However, it should be remarked that the apparent transitions do not represent any transition in the system; those transitions are the two conventional transitions discussed above. The apparent transitions represent our desire to compare two distinct states. This is like comparing the supercooled liquid with the crystal at the same temperature and pressure. Therefore, a discontinuity in the Gibbs free energy is not a violation of the principle of continuity discussed in [3].

We will consider all of the above glass transitions later when we discuss the evaluation of the Prigogine-Defay ratio [9–13] in Sect. VIII. In this ratio, a non-equilibrium state is compared with the equilibrium supercooled liquid state along ABF. In the classic approach adopted by Simon [6, 14], the temperature range  $(T_{0gG}(P_0), T_{0g}(P_0))$  is shrunk to a point, either by considering the apparent glass transition at  $T_{0g}^{(A)}(P_0)$ , or by comparing the glass state at D with the supercooled liquid L at B. The latter amounts to neglecting the segment BD from consideration. We will avoid this ad-hoc approach in this work. The only possible scenario, where Simon’s approach is meaningful is that of the *ideal glass transition* [5, and references thererin], in the limit the cooling rate  $r \rightarrow 0$ . In this limiting case, the crossover region BD disappears and the ideal glass IGL emerges directly out of the L at the ideal glass transition temperature  $T_{0IG}$ . This is a conventional continuous transition between the two stationary states IGL and L, both of which remain in equilibrium with the medium at  $T_0, P_0$ . There is no need to invoke any internal variable  $\mathbf{I}$  to describe the ideal glass; the observable  $\mathbf{X}$  is sufficient for the investigation of the ideal glass transition. We will revisit this point later in Sect. VIII.

### III. SOME USEFUL MATHEMATICAL TOOLS

#### A. Jacobian method

Jacobians [15] will be found extremely useful in this work just as they are found useful in equilibrium thermodynamics [4]; see also [16–18]. The  $n$ -th order Jacobian of  $u_1, u_2, \dots, u_n$

with respect to  $x_1, x_2, \dots, x_n$  is the  $n \times n$  determinant of the matrix formed by  $\partial u_k / \partial x_l$ :

$$\frac{\partial(u_1, u_2, \dots, u_n)}{\partial(x_1, x_2, \dots, x_n)} \equiv \begin{vmatrix} \frac{\partial u_1}{\partial x_1} & \frac{\partial u_1}{\partial x_2} & \dots & \frac{\partial u_1}{\partial x_n} \\ \frac{\partial u_2}{\partial x_1} & \frac{\partial u_2}{\partial x_2} & \dots & \frac{\partial u_2}{\partial x_n} \\ \vdots & \vdots & \ddots & \vdots \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial u_n}{\partial x_1} & \frac{\partial u_n}{\partial x_2} & \dots & \frac{\partial u_n}{\partial x_n} \end{vmatrix}.$$

It is clear from the properties of the determinant that

1. The Jacobian vanishes if any two  $u$ 's are identical

$$\frac{\partial(u_1, u_2, \dots, u_i, u_i \dots, u_n)}{\partial(x_1, x_2, \dots, x_i, x_{i+1} \dots, x_n)} = 0.$$

2. If  $u_i$  and  $u_{i+1}$  interchange their order, the Jacobian changes its sign

$$\frac{\partial(u_1, u_2, \dots, u_{i+1}, u_i \dots, u_n)}{\partial(x_1, x_2, \dots, x_i, x_{i+1} \dots, x_n)} = -\frac{\partial(u_1, u_2, \dots, u_i, u_{i+1} \dots, u_n)}{\partial(x_1, x_2, \dots, x_i, x_{i+1} \dots, x_n)}.$$

3. If any  $u_i$  is equal to  $x_i$ , the  $n$ -th order Jacobian reduces to a  $(n-1)$ -th order Jacobian formed by derivatives at fixed  $x_i$ . For example, for  $n=2$ , we have

$$\frac{\partial(u_1, x_2)}{\partial(x_1, x_2)} = \left( \frac{\partial u_1}{\partial x_1} \right)_{x_2}.$$

When we consider compound transformations  $(x_1, x_2, \dots, x_n) \rightarrow (u_1, u_2, \dots, u_n) \rightarrow (v_1, v_2, \dots, v_n)$ , the resulting Jacobian is the product of the two Jacobians:

$$\frac{\partial(v_1, v_2, \dots, v_n)}{\partial(u_1, u_2, \dots, u_n)} \cdot \frac{\partial(u_1, u_2, \dots, u_n)}{\partial(x_1, x_2, \dots, x_n)} = \frac{\partial(v_1, v_2, \dots, v_n)}{\partial(x_1, x_2, \dots, x_n)}.$$

The definition of a Jacobian can lead to some interesting permutation rules as the following examples illustrate. Consider a second order Jacobian  $\partial(u_1, u_2) / \partial(x_1, x_2) = (\partial u_1 / \partial x_1)(\partial u_2 / \partial x_2) - (\partial u_1 / \partial x_2)(\partial u_2 / \partial x_1)$ , which can be rearranged as

$$\frac{\partial(u_1, u_2)}{\partial(x_1, x_2)} \frac{\partial(x_1, x_2)}{\partial(x_1, x_2)} + \frac{\partial(u_2, x_1)}{\partial(x_1, x_2)} \frac{\partial(u_1, x_2)}{\partial(x_1, x_2)} + \frac{\partial(x_1, u_1)}{\partial(x_1, x_2)} \frac{\partial(u_2, x_2)}{\partial(x_1, x_2)} = 0.$$

This can be symbolically written as

$$\partial(u_1, u_2)(x_1, x_2) + \partial(u_2, x_1)\partial(u_1, x_2) + \partial(x_1, u_1)\partial(u_2, x_2) = 0 \quad (11)$$

by suppressing the common denominator in each term. The result expresses the cyclic permutation of  $u_1, u_2, x_1$  in the three terms with the remaining variable  $x_2$  in the same place in all terms. As a second example, consider some quantity  $u$  as a function of three variables  $x, y$ , and  $z$  and consider the following relation between the partial derivatives:

$$\left(\frac{\partial u}{\partial x}\right)_y = \left(\frac{\partial u}{\partial x}\right)_{y,z} + \left(\frac{\partial u}{\partial z}\right)_{x,y} \left(\frac{\partial z}{\partial x}\right)_y. \quad (12)$$

In terms of Jacobians, it can be written as

$$\frac{\partial(u, y)}{\partial(x, y)} = \frac{\partial(u, y, z)}{\partial(x, y, z)} + \frac{\partial(u, x, y)}{\partial(z, x, y)} \frac{\partial(z, y)}{\partial(x, y)}, \quad (13)$$

which simplifies to

$$\partial(x, y, z)\partial(u, y) = \partial(y, z, u)\partial(x, y) + \partial(z, u, x)\partial(y, y) + \partial(u, x, y)\partial(z, y), \quad (14)$$

where we have added a vanishing second term on the right because  $\partial(y, y) = 0$ . This relation is easily constructed by considering the cyclic permutation of

$$x, y, z, u$$

by taking three consecutive terms at a time for the 3-Jacobians, with the remaining variable yielding the 2-Jacobians in which the second entry is the variable  $y$ , the variable that is held fixed in all derivatives in Eq. (12). The ordering  $x, y, z$  in  $x, y, z, u$  is determined by the denominator 3-Jacobian in the first term on the right in Eq. (13). By writing all the 3-Jacobians in the non-vanishing terms in Eq. (14) so that  $y$  is the second entry, and then suppressing the second entry, we obtain the following relation

$$\partial(x, z)\partial(u, y) + \partial(z, u)\partial(x, y) + \partial(u, x)\partial(z, y) = 0,$$

which is identical to the relation in Eq. (11) if we identify  $u_1$  with  $x$ ,  $u_2$  with  $z$ ,  $x_1$  with  $u$  and  $x_2$  with  $y$ .

We will use the Jacobians and their properties to first re-express the Maxwell relations as follows

$$\begin{aligned} \frac{\partial(T_0, S, N)}{\partial(V, S, N)} &= \frac{\partial(P_0, V, N)}{\partial(V, S, N)}, & \frac{\partial(T_0, S, N)}{\partial(P_0, S, N)} &= \frac{\partial(P_0, V, N)}{\partial(P_0, S, N)}, \\ \frac{\partial(P_0, V, N)}{\partial(T_0, V, N)} &= \frac{\partial(T_0, S, N)}{\partial(T_0, V, N)}, & \frac{\partial(T_0, S, N)}{\partial(P_0, T_0, N)} &= \frac{\partial(P_0, V, N)}{\partial(P_0, T_0, N)}. \end{aligned} \quad (15)$$

We now see a very important consequence of the use of the Jacobians. All four Maxwell relations use the same numerators  $\partial(T_0, S, N)$  and  $\partial(P_0, V, N)$ . They use different denominators. Thus, they can all be combined into one compact relation that can be simply written as

$$\partial(T_0, S, N) \equiv \partial(P_0, V, N). \quad (16)$$

Here, the relation only has a meaning if each side is divided by one of the possible denominators  $\partial(V, S, N)$ ,  $\partial(P_0, S, N)$ ,  $\partial(T_0, V, N)$  and  $\partial(P_0, T_0, N)$  on both sides.

## B. Considerations in a Subspace

It is very common to consider a function  $F(x, y, z)$  in a subspace consisting of  $x, y$ . This requires manipulating a 3-Jacobians to construct a 2-Jacobians. of its argument. Thus, we may consider the 2-Jacobian

$$\frac{\partial(F, y)}{\partial(x, y)},$$

even though  $F$  also depends on  $z$ . We can manipulate such Jacobians in the normal way. For example, we can express it as

$$\left( \frac{\partial F}{\partial x} \right)_y = \frac{\partial(F, y)}{\partial(x, y)} = - \frac{\partial(F, y)}{\partial(K, x)} \frac{\partial(x, K)}{\partial(x, y)} = - \left( \frac{\partial K}{\partial y} \right)_x \frac{\partial(F, y)}{\partial(K, x)}, \quad (17)$$

where  $K(x, y, z)$  is another function. The derivation is tedious and has been supplied in the Appendix. The situation can be generalized to many variables  $z_1, z_2, \dots$  without much complications. We will not do this here.

## C. Some Transformation Rules

Let us consider a derivative of some quantity  $R$  either with respect to  $T$  or  $P$  in case A below or at fixed  $T$  or  $P$  in case B below, which we wish to express as a derivative involving  $T_0, P_0$  that are manipulated by the observer.

- A. The derivative is at fixed  $\mathbf{U}$ , where  $\mathbf{U}$  has any two different elements from  $E, V, S, \xi, P_0$  and  $T_0$ .

We write the derivative as

$$\left(\frac{\partial R}{\partial T}\right)_{U_1, U_2} \equiv \frac{\partial(R, U_1, U_2)}{\partial(T, U_1, U_2)} = \frac{\partial(R, U_1, U_2)}{\partial(T_0, U_1, U_2)} \frac{\partial(T_0, U_1, U_2)}{\partial(T, U_1, U_2)} = \left(\frac{\partial R}{\partial T_0}\right)_{U_1, U_2} / \left(\frac{\partial T}{\partial T_0}\right)_{U_1, U_2}. \quad (18)$$

Similarly, we have

$$\left(\frac{\partial R}{\partial P}\right)_{U_1, U_2} \equiv \frac{\partial(R, U_1, U_2)}{\partial(P, U_1, U_2)} = \frac{\partial(R, U_1, U_2)}{\partial(P_0, U_1, U_2)} \frac{\partial(P_0, U_1, U_2)}{\partial(P, U_1, U_2)} = \left(\frac{\partial R}{\partial P_0}\right)_{U_1, U_2} / \left(\frac{\partial P}{\partial P_0}\right)_{U_1, U_2}. \quad (19)$$

B. Let us consider a derivative with respect to  $T_0$  at fixed  $U_2 = P$  or  $T$  ( $U_{20} = P_0$  or  $T_0$ , as the case may be), but  $U_1$  is any element from  $E, V, S, \xi, P_0$  and  $T_0$ :

$$\left(\frac{\partial R}{\partial T_0}\right)_{U_1, U_2} \equiv \frac{\partial(R, U_1, U_2)}{\partial(T_0, U_1, U_{20})} \frac{\partial(T_0, U_1, U_{20})}{\partial(T_0, U_1, U_2)} = \frac{\partial(R, U_2, U_1)}{\partial(T_0, U_{20}, U_1)} / \left(\frac{\partial U_2}{\partial U_{20}}\right)_{U_1, U_2}. \quad (20)$$

Similarly,

$$\left(\frac{\partial R}{\partial P_0}\right)_{U_1, U_2} \equiv \frac{\partial(R, U_1, U_2)}{\partial(P_0, U_1, U_{20})} \frac{\partial(P_0, U_1, U_{20})}{\partial(P_0, U_1, U_2)} = \frac{\partial(R, U_2, U_1)}{\partial(P_0, U_{20}, U_1)} / \left(\frac{\partial U_2}{\partial U_{20}}\right)_{U_1, U_2}. \quad (21)$$

Let us now consider a derivative with respect to  $T$  at fixed  $P$  or with respect to  $P$  at fixed  $T$ ; the derivative is at fixed  $U_1$ , where  $U_1$  is any element from  $E, V, S, \xi, P_0$  and  $T_0$ .

$$\left(\frac{\partial R}{\partial T}\right)_{U_1, P} \equiv \frac{\partial(R, U_1, P)}{\partial(T, U_1, P)} = \frac{\partial(R, U_1, P)}{\partial(T_0, U_1, P_0)} / \frac{\partial(T, U_1, P)}{\partial(T_0, U_1, P_0)}. \quad (22)$$

Similarly,

$$\left(\frac{\partial R}{\partial P}\right)_{U_1, T} \equiv \frac{\partial(R, U_1, T)}{\partial(P, U_1, T)} = \frac{\partial((R, U_1, T))}{\partial(T_0, U_1, P_0)} / \frac{\partial(P, U_1, T)}{\partial(T_0, U_1, P_0)}. \quad (23)$$

## IV. THERMODYNAMIC POTENTIALS AND DIFFERENTIALS

### A. Equilibrium

The forms of most useful thermodynamic potentials such as the enthalpy  $H$ , the Helmholtz free energy  $F$ , and the Gibbs free energy  $G$  of a system  $\Sigma$  in equilibrium are well known and are given in terms of the energy  $E(S, V, N)$  as

$$H = E + P_0V, \quad F = E - T_0S, \quad G = E - T_0S + P_0V, \quad (24)$$

where  $T_0, P_0$  are the temperature and pressure of the system; they are also the temperature and/or pressure of the medium, depending on the medium  $\tilde{\Sigma}$ . Here, we are considering

a system with fixed number of particles. For the enthalpy, the medium  $\tilde{\Sigma}(P_0)$  containing the system exerts a fixed pressure  $P_0$ . For the Helmholtz free energy, the medium  $\tilde{\Sigma}(T_0)$  containing the system creates a fixed temperature  $T_0$ . For the Gibbs free energy, the medium  $\tilde{\Sigma}(T_0, P_0)$  containing the system exerts a fixed pressure  $P_0$  and creates a fixed temperature  $T_0$ . The potentials are Legendre transforms in that the potentials are functions of the fields  $(T_0, P_0)$  rather than the observables  $(E, V)$  as the case may be. These potentials have the desired property that they attain their minimum when the system is in equilibrium, as discussed in I.

## B. Internal Equilibrium

When the system is in internal equilibrium, we find from the Gibbs fundamental relation for fixed  $N$ , which is obtained from setting  $dN = 0$  in Eq. (5):

$$dE = TdS - PdV - Ad\xi, \quad (25)$$

where we have also introduced a single internal variable  $\xi$  to allow us to discuss non-equilibrium systems that are not in equilibrium with their medium but are in internal equilibrium. The consideration of many internal variables is to simply replace

$$Ad\xi \rightarrow \mathbf{A} \cdot d\xi,$$

and will not cause any extra complication. Thus, we will mostly consider a single internal variable, but the extension to many internal variables is trivial.

We are no longer going to exhibit the time-dependence in these variables for the sake of notational simplicity of. Let us return to Eq. (25). It should be compared with Eq. (6) which contains  $T_0, P_0$ . We rewrite Eq. (25) to show the non-equilibrium contribution explicitly:

$$dE = T_0 dS - P_0 dV + (T - T_0) dS - (P - P_0) dV - Ad\xi. \quad (26)$$

The last two terms are due to the non-equilibrium nature of the system in internal equilibrium. It is now easy to see that

$$\begin{aligned} dH &= T_0 dS + V dP_0 + (T - T_0) dS - (P - P_0) dV - Ad\xi, \\ dF &= -S dT_0 - P_0 dV + (T - T_0) dS - (P - P_0) dV - Ad\xi, \\ dG &= -S dT_0 + V dP_0 + (T - T_0) dS - (P - P_0) dV - Ad\xi. \end{aligned} \quad (27)$$

These potentials correspond to  $\xi$  as an independent variable of the potential. One can make a transformation of these potentials to potentials in which the conjugate field  $A_0$  of the medium is the independent variable by adding  $A_0\xi$ . The resulting potentials will be denoted by a superscript A on the potential:

$$E^A = E + A_0\xi, H^A = H + A_0\xi, F^A = F + A_0\xi, G^A = G + A_0\xi.$$

However, as discussed in II,  $A_0 = 0$ . Thus, there is no difference in the values of the two potentials and the transformation is of no use. In equilibrium, the internal fields  $T, P$  attain their equilibrium values  $T_0, P_0$  of the medium, and the affinity  $A$  vanishes identically because of  $A_0 = 0$ .

## V. MAXWELL RELATIONS FOR SYSTEMS IN INTERNAL EQUILIBRIUM

From now on, we will always consider the case of a constant  $N$ . Therefore, we will no longer exhibit it anymore. The Maxwell relation in Eq. (16) will then be denoted simply as  $\partial(T_0, S) \equiv \partial(P_0, V)$ . The field parameters that appear in the Maxwell relation are the parameters  $T_0, P_0$  of the medium, which because of the existence of equilibrium also represent the field parameters of the system. The Maxwell relation is a relation between the pairs  $T_0, S$  and  $P_0, V$ , each pair formed by the extensive variable and its conjugate field. We will call these pairs conjugate pairs in this work. For a system described by only two conjugate pairs, there is only one possible Maxwell relation. For a system described by three conjugate pairs, there will be three different Maxwell relations between them. For a system described by  $k$  conjugate pairs, there will be  $k(k - 1)/2$  different Maxwell relations.

As the system in internal equilibrium is very similar in many respects with an equilibrium system as discussed in I and II, there may be analogs of the Maxwell relations for systems in internal equilibrium. The question then arises as to the field parameters that must appear in the Maxwell relations when the system is not in equilibrium, but only in internal equilibrium. We now turn to answer this question. Because of the absence of equilibrium, we must now also include the internal variable  $\xi$  in the discussion. Thus, we expect three different Maxwell relations between

### A. Maxwell relation $\partial(T, S, \xi) \equiv \partial(P, V, \xi)$ at fixed $\xi$

We start with Eq. (25) and observe that

$$\left(\frac{\partial E}{\partial S}\right)_{V,\xi} = T, \left(\frac{\partial E}{\partial V}\right)_{S,\xi} = -P, \left(\frac{\partial E}{\partial \xi}\right)_{S,V} = -A. \quad (28)$$

Using the first two derivative at fixed  $\xi$ , we find that

$$\left(\frac{\partial^2 E}{\partial V \partial S}\right)_\xi = \left(\frac{\partial T}{\partial V}\right)_{S,\xi}, \quad \left(\frac{\partial^2 E}{\partial S \partial V}\right)_\xi = -\left(\frac{\partial P}{\partial S}\right)_{V,\xi}.$$

As we are allowed to interchange the order of derivatives in the above cross derivative, we have

$$\left(\frac{\partial T}{\partial V}\right)_{S,\xi} = -\left(\frac{\partial P}{\partial S}\right)_{V,\xi},$$

which can be written using Jacobians as

$$\frac{\partial(T, S, \xi)}{\partial(S, V, \xi)} = \frac{\partial(P, V, \xi)}{\partial(S, V, \xi)}.$$

This suggests the existence of the Maxwell relation  $\partial(T, S, \xi) = \partial(P, V, \xi)$  between the conjugate pairs  $T, S$  and  $P, V$  at fixed  $\xi$ . To check its validity for other potentials with  $\xi$  as an independent variable, we consider the differential  $dG$  in Eq. (27) and note that

$$\begin{aligned} \left(\frac{\partial G}{\partial T_0}\right)_{P_0,\xi} &= -S + (T - T_0) \left(\frac{\partial S}{\partial T_0}\right)_{P_0,\xi} + (P_0 - P) \left(\frac{\partial V}{\partial T_0}\right)_{P_0,\xi}, \\ \left(\frac{\partial G}{\partial P_0}\right)_{T_0,\xi} &= V + (T - T_0) \left(\frac{\partial S}{\partial P_0}\right)_{T_0,\xi} + (P_0 - P) \left(\frac{\partial V}{\partial T_0}\right)_{P_0,\xi}. \end{aligned}$$

We use these derivatives to evaluate the cross derivative  $(\partial^2 G / \partial P_0 \partial T_0)_\xi$  to conclude that

$$\begin{aligned} &-\left(\frac{\partial S}{\partial P_0}\right)_{T_0,\xi} + (T - T_0) \left(\frac{\partial^2 S}{\partial T_0 \partial P_0}\right)_\xi + \left(\frac{\partial T}{\partial P_0}\right)_{T_0,\xi} \left(\frac{\partial S}{\partial T_0}\right)_{P_0,\xi} \\ &+ (P_0 - P) \left(\frac{\partial^2 V}{\partial P_0 \partial T_0}\right)_\xi + \left(\frac{\partial V}{\partial T_0}\right)_{P_0,\xi} - \left(\frac{\partial P}{\partial P_0}\right)_{T_0,\xi} \left(\frac{\partial V}{\partial T_0}\right)_{P_0,\xi} \\ &= \left(\frac{\partial V}{\partial T_0}\right)_{P_0,\xi} + (T - T_0) \left(\frac{\partial^2 S}{\partial P_0 \partial T_0}\right)_\xi + \left(\frac{\partial T}{\partial T_0}\right)_{P_0,\xi} \left(\frac{\partial S}{\partial P_0}\right)_{T_0,\xi} \\ &+ (P_0 - P) \left(\frac{\partial^2 V}{\partial P_0 \partial T_0}\right)_\xi - \left(\frac{\partial S}{\partial P_0}\right)_{T_0,\xi} - \left(\frac{\partial P}{\partial T_0}\right)_{P_0,\xi} \left(\frac{\partial V}{\partial P_0}\right)_{T_0,\xi}. \end{aligned}$$

This is simplified to yield

$$\left(\frac{\partial T}{\partial P_0}\right)_{T_0,\xi} \left(\frac{\partial S}{\partial T_0}\right)_{P_0,\xi} - \left(\frac{\partial T}{\partial T_0}\right)_{P_0,\xi} \left(\frac{\partial S}{\partial P_0}\right)_{T_0,\xi} = \left(\frac{\partial P}{\partial P_0}\right)_{T_0,\xi} \left(\frac{\partial V}{\partial T_0}\right)_{P_0,\xi} - \left(\frac{\partial P}{\partial T_0}\right)_{T_0,\xi} \left(\frac{\partial V}{\partial P_0}\right)_{P_0,\xi}.$$

In terms of the Jacobians, this can be written as

$$\frac{\partial(T, S, \xi)}{\partial(T_0, P_0, \xi)} = \frac{\partial(P, V, \xi)}{\partial(T_0, P_0, \xi)},$$

thus justifying the Maxwell relation

$$\partial(T, S, \xi) = \partial(P, V, \xi) \quad (29)$$

at fixed  $\xi$ . This relation must be satisfied at every point on the curve ABDE that describes the vitrification process. This Maxwell relation turns into the identity

$$\frac{\partial(T, S, \xi)}{\partial(P_0, S, \xi)} = \frac{\partial(P, V, \xi)}{\partial(P_0, S, \xi)}$$

for the enthalpy and

$$\frac{\partial(T, S, \xi)}{\partial(T_0, V, \xi)} = \frac{\partial(P, V, \xi)}{\partial(T_0, V, \xi)} \quad (30)$$

for the Helmholtz free energy, and are easily verified.

## B. Maxwell relation $\partial(T, S, V) \equiv \partial(A, \xi, V)$ at fixed $V$

We again start with Eqs. (25) and (28), and evaluate the cross derivative  $(\partial^2 E / \partial S \partial \xi)_V$  to obtain

$$\left(\frac{\partial^2 E}{\partial \xi \partial S}\right)_V = \left(\frac{\partial T}{\partial \xi}\right)_{S,V}, \quad \left(\frac{\partial^2 E}{\partial S \partial \xi}\right)_V = - \left(\frac{\partial A}{\partial S}\right)_{V,\xi}.$$

We thus have

$$\left(\frac{\partial T}{\partial \xi}\right)_{S,V} = - \left(\frac{\partial A}{\partial S}\right)_{V,\xi},$$

which can be written using Jacobians as

$$\frac{\partial(T, S, V)}{\partial(\xi, S, V)} = \frac{\partial(A, \xi, V)}{\partial(\xi, S, V)}.$$

This suggests the existence of the Maxwell relation  $\partial(T, S, V) = \partial(A, \xi, V)$  between the conjugate pairs  $T, S$  and  $A, \xi$  at fixed  $V$ . To check its validity for other potentials with  $V$  as an independent variable, we consider the differential  $dF$  in Eq. (27) and note that

$$\begin{aligned}\left(\frac{\partial F}{\partial T_0}\right)_{V,\xi} &= -S + (T - T_0) \left(\frac{\partial S}{\partial T_0}\right)_{V,\xi} \\ \left(\frac{\partial F}{\partial \xi}\right)_{V,T_0} &= -A + (T - T_0) \left(\frac{\partial S}{\partial \xi}\right)_{V,T_0}.\end{aligned}$$

We now evaluate the cross derivative  $(\partial^2 F / \partial \xi \partial T_0)_V$  and obtain the equality

$$\begin{aligned}& - \left(\frac{\partial S}{\partial \xi}\right)_{T_0,V} + \left(\frac{\partial S}{\partial T_0}\right)_{V,\xi} \left(\frac{\partial T}{\partial \xi}\right)_{T_0,V} + (T - T_0) \left(\frac{\partial^2 S}{\partial \xi \partial T_0}\right)_V \\ &= - \left(\frac{\partial A}{\partial T_0}\right)_{V,\xi} + \left[ \left(\frac{\partial T}{\partial T_0}\right)_{V,\xi} - 1 \right] \left(\frac{\partial S}{\partial \xi}\right)_{T_0,V} + (T - T_0) \left(\frac{\partial^2 S}{\partial \xi \partial T_0}\right)_V,\end{aligned}$$

which leads to the relation

$$\frac{\partial(A, \xi, V)}{\partial(T_0, \xi, V)} = \frac{\partial(T, S, V)}{\partial(T_0, \xi, V)}.$$

This confirms that the Maxwell relation between the conjugate pairs  $T, S$  and  $A, \xi$  at fixed  $V$  is the following:

$$\partial(T, S, V) = \partial(A, \xi, V). \quad (31)$$

### C. Maxwell Relation $\partial(P, V, S) \equiv \partial(A, \xi, S)$ at fixed $S$

We again start with Eqs. (25) and (28), and evaluate the cross derivative  $(\partial^2 E / \partial V \partial \xi)_S$  to obtain

$$\left(\frac{\partial^2 E}{\partial \xi \partial V}\right)_S = - \left(\frac{\partial P}{\partial \xi}\right)_{S,V}, \quad \left(\frac{\partial^2 E}{\partial V \partial \xi}\right)_S = - \left(\frac{\partial A}{\partial V}\right)_{S,\xi}.$$

We thus have

$$\left(\frac{\partial P}{\partial \xi}\right)_{S,V} = \left(\frac{\partial A}{\partial V}\right)_{S,\xi},$$

which can be written using Jacobians as

$$\frac{\partial(P, V, S)}{\partial(\xi, V, S)} = - \frac{\partial(A, \xi, S)}{\partial(\xi, V, S)}.$$

This suggests the existence of the Maxwell relation  $\partial(P, V, S) = -\partial(A, \xi, S)$  between the conjugate pairs  $P, V$  and  $A, \xi$  at fixed  $S$ . To check its validity for other potentials with  $S$

as an independent variable, we consider the differential  $dH$  in Eq. (27) and note that

$$\begin{aligned}\left(\frac{\partial H}{\partial P_0}\right)_{S,\xi} &= V - (P - P_0) \left(\frac{\partial V}{\partial P_0}\right)_{S,\xi} \\ \left(\frac{\partial F}{\partial \xi}\right)_{S,P_0} &= -A - (P - P_0) \left(\frac{\partial V}{\partial \xi}\right)_{S,T_0}.\end{aligned}$$

We now evaluate the cross derivative  $(\partial^2 H / \partial \xi \partial P_0)_S$  and obtain the equality

$$\begin{aligned}&\left(\frac{\partial V}{\partial \xi}\right)_{P_0,S} - \left(\frac{\partial V}{\partial P_0}\right)_{S,\xi} \left(\frac{\partial P}{\partial \xi}\right)_{P_0,S} - (P - P_0) \left(\frac{\partial^2 V}{\partial \xi \partial P_0}\right)_S \\ &= - \left(\frac{\partial A}{\partial P_0}\right)_{S,\xi} - \left[\left(\frac{\partial P}{\partial P_0}\right)_{S,\xi} - 1\right] \left(\frac{\partial V}{\partial \xi}\right)_{P_0,S} - (P - P_0) \left(\frac{\partial^2 V}{\partial \xi \partial P_0}\right)_S,\end{aligned}$$

which leads to the relation

$$\frac{\partial(A, \xi, S)}{\partial(P_0, \xi, S)} = -\frac{\partial(P, V, S)}{\partial(P_0, \xi, S)}.$$

This confirms that the Maxwell relation between the conjugate pairs  $P, V$  and  $A, \xi$  at fixed  $S$  is the following:

$$\partial(P, V, S) = -\partial(A, \xi, S). \quad (32)$$

One can easily check that this Maxwell relation also works with other thermodynamic potentials like  $F$  and  $G$ . We will satisfy ourselves by giving the demonstration for  $F$  only. The natural variables for  $F$  are  $T_0, \xi$  and  $V$ ; however, instead of using  $V$  as the independent variable, we will use  $S$  as the independent variable so that it can be held fixed. For constant  $S$ , the differential  $dF$  from Eq. (27) reduces to

$$dF|_S = -SdT_0 - PdV - Ad\xi,$$

so that

$$\begin{aligned}\left(\frac{\partial F}{\partial T_0}\right)_{S,\xi} &= -S - P \left(\frac{\partial V}{\partial T_0}\right)_{S,\xi} \\ \left(\frac{\partial F}{\partial \xi}\right)_{S,T_0} &= -A - P \left(\frac{\partial V}{\partial \xi}\right)_{S,T_0}.\end{aligned}$$

Now evaluating the cross derivative  $(\partial^2 F / \partial \xi \partial T_0)_S$ , we find that

$$\begin{aligned}&- \left(\frac{\partial A}{\partial T_0}\right)_{S,\xi} - \left(\frac{\partial P}{\partial T_0}\right)_{S,\xi} \left(\frac{\partial V}{\partial \xi}\right)_{T_0,S} - P \left(\frac{\partial^2 V}{\partial \xi \partial T_0}\right)_S \\ &= - \left(\frac{\partial V}{\partial T_0}\right)_{S,\xi} \left(\frac{\partial P}{\partial \xi}\right)_{T_0,S} - P \left(\frac{\partial^2 V}{\partial \xi \partial P_0}\right)_S.\end{aligned}$$

This now immediately leads to

$$\frac{\partial(A, \xi, S)}{\partial(T_0, \xi, S)} = -\frac{\partial(P, V, S)}{\partial(T_0, \xi, S)}, \quad (33)$$

and confirms our claim that the Maxwell relation is given by Eq. (32).

#### D. General Maxwell Relations with system variables only

We wish to emphasize that the Maxwell relation in Eq. (33) requires keeping  $S$  fixed so that we must divide Eq. (32) by  $\partial(T_0, \xi, S)$  on both sides. We must not use the independent variables  $T_0, \xi$  and  $V$  of  $F$  for the division and keep  $T_0$  fixed. This will not give be a Maxwell relation. We demonstrate this explicitly by evaluating  $(\partial^2 F / \partial \xi \partial V)_{T_0}$  two different ways and equating the results. A simple calculation yields

$$\begin{aligned} & - \left( \frac{\partial P}{\partial \xi} \right)_{V, T_0} + \left( \frac{\partial S}{\partial V} \right)_{T_0, \xi} \left( \frac{\partial T}{\partial \xi} \right)_{V, T_0} + (T - T_0) \left( \frac{\partial^2 S}{\partial V \partial \xi} \right)_{T_0} \\ &= - \left( \frac{\partial A}{\partial V} \right)_{T_0, \xi} + \left( \frac{\partial S}{\partial \xi} \right)_{V, T_0} \left( \frac{\partial T}{\partial V} \right)_{T_0, \xi} + (T - T_0) \left( \frac{\partial^2 S}{\partial V \partial \xi} \right)_{T_0}. \end{aligned}$$

In terms of Jacobians, the above equation can be rewritten as

$$\frac{\partial(A, \xi, T_0)}{\partial(V, \xi, T_0)} = -\frac{\partial(P, V, T_0)}{\partial(V, \xi, T_0)} + \frac{\partial(T, S, T_0)}{\partial(V, \xi, T_0)}. \quad (34)$$

This relation from the cross derivative requires keeping  $T_0$  fixed. However,  $T_0$  characterizes the medium and only indirectly characterizes the system in internal equilibrium. In a similar way, using the cross derivatives of the Gibbs free energy at fixed  $T_0$ , and at fixed  $P_0$ , we find the following relations:

$$\frac{\partial(A, \xi, P_0)}{\partial(T_0, P_0, \xi)} = \frac{\partial(T, S, P_0)}{\partial(T_0, P_0, \xi)} + \frac{\partial(P, V, P_0)}{\partial(T_0, P_0, \xi)}, \quad \frac{\partial(A, \xi, T_0)}{\partial(T_0, P_0, \xi)} = \frac{\partial(P, V, T_0)}{\partial(T_0, P_0, \xi)} - \frac{\partial(T, S, T_0)}{\partial(T_0, P_0, \xi)}. \quad (35)$$

We now wish to observe that the Maxwell relations appear only when we keep the quantities of the system  $T, P, S, V, A$ , or  $\xi$  fixed. We have already seen the Maxwell relations with fixed  $S, V$ , and  $\xi$ . We will now consider keeping  $T$  fixed to demonstrate our point. For fixed  $T$ , we obtain the following Maxwell relation

$$\frac{\partial(A, \xi, T)}{\partial(T_0, \xi, T)} = -\frac{\partial(P, V, T)}{\partial(T_0, \xi, T)}, \quad (36)$$

as can easily be checked by evaluating the cross derivative  $(\partial^2 F / \partial \xi \partial T_0)_T$  at fixed  $T$ . The calculation is identical to that carried out in obtaining Eq. (33). One can easily check that keeping  $P$  or  $A$  also gives us new Maxwell relations

$$\frac{\partial(A, \xi, P)}{\partial(T_0, \xi, P)} = \frac{\partial(T, S, P)}{\partial(T_0, \xi, P)}, \frac{\partial(T, S, A)}{\partial(\xi, T_0, A)} = -\frac{\partial(P, V, A)}{\partial(T_0, \xi, A)}.$$

## VI. CLAUSIUS-CLAPEYRON RELATION

As a system in internal equilibrium is not very different from that in equilibrium, except that its Gibbs free energy  $G(t)$  continuously decreases until it reaches equilibrium with the medium, it is possible for the system to exist in two distinct phases that have the same Gibbs free energy at some instant. Such a non-equilibrium phase transition situation will arise, for example, when an isotropic supercooled liquid can turn into a liquid crystal phase. This is not a novel idea as there are several attempts in the literature [19–22, and references therin] where such non-equilibrium phase transitions have been investigated. Therefore, let us now consider the possibility of the system being in two different phases at some time. As experiments are carried out by controlling observables only and not the internal variables, it is important to consider thermodynamic quantities as a function of  $\mathbf{X}$  only, and not of  $\mathbf{X}, \mathbf{I}$  in all cases. Restricting ourselves to a single internal variable  $\xi$ , and to  $E$  and  $V$ , we will treat thermodynamic quantities not only as a function of three independent variables, but will also have the need to consider them as a function of observables or associated fields  $T_0, P_0$ . In particular, the Clausius-Clapeyron relation is obtained in the  $T_0$ - $P_0$  plane, a subspace; see Sect. III B.

Let us consider the two phases, which we denote by 1 and 2, in the system. We will use subscripts 1 and 2 to refer to the quantities in the two phases. In internal equilibrium, the entropy  $S$  of the system is a function of the averages  $\mathbf{X}(t), \mathbf{I}(t)$  along with the fixed number of particles  $N$ . It is important to include  $N$  in our consideration as the two phases will contain number of particles  $N_1$  and  $N_2$  that are not constant, except in equilibrium. Obviously,

$$\mathbf{X}(t) = \mathbf{X}_1(t) + \mathbf{X}_2(t), \mathbf{I}(t) = \mathbf{I}_1(t) + \mathbf{I}_2(t), N = N_1(t) + N_2(t).$$

Then, we can express the entropy of the system as a sum over the two phases:

$$S(\mathbf{X}(t), \mathbf{I}(t), N) = S_1(\mathbf{X}_1(t), \mathbf{I}_1(t), N_1(t)) + S_2(\mathbf{X}_2(t), \mathbf{I}_2(t), N_2(t)),$$

which takes its maximum possible value for given  $\mathbf{X}(t), \mathbf{I}(t), N$  in internal equilibrium. Thus,

$$dS(\mathbf{X}(t), \mathbf{I}(t), N) = dS_1(\mathbf{X}_1(t), \mathbf{I}_1(t), N_1(t)) + dS_2(\mathbf{X}_2(t), \mathbf{I}_2(t), N_2(t)) = 0$$

in internal equilibrium. This can only happen if

$$\mathbf{y}_1(t) = \mathbf{y}_2(t), \quad \mathbf{a}_1(t) = \mathbf{a}_2(t), \quad \mu_1(t)/T_1(t) = \mu_2(t)/T_2(t);$$

see Eqs. (1), (3) and (2).

For the restricted case under consideration, this results in the equality

$$T_1(t) = T_2(t), \quad P_1(t) = P_2(t), \quad \mu_1(t) = \mu_2(t), \quad A_1(t) = A_2(t)$$

for the internal fields and affinity along the coexistence of the two phases. It also follows from the continuity of the Gibbs free energy [1] that the Gibbs free energies of the two pure phases ( $N_1 = N$  and  $N_2 = N$ ) must be equal at the coexistence. We will only consider the two pure phases below, and not a mixture of the two. As the numbers of particles in the two pure phases are constant, we will no longer consider them anymore in the discussion.

We now consider the  $T_0$ - $P_0$  plane, relevant for the observation of coexistence. Since the Gibbs free energy is continuous along the transition line,

$$\Delta G(T_0, P_0(T_0)) = 0$$

where  $P_0(T_0)$  is the pressure along the transition line. Thus,

$$d\Delta G = \Delta \left( \frac{\partial G}{\partial T_0} \right)_{P_0} dT_0 + \Delta \left( \frac{\partial G}{\partial P_0} \right)_{T_0} dP_0.$$

Using  $d\Delta G = 0$  yields

$$\left. \frac{dT_0}{dP_0} \right|_{\text{coex}} \Delta \left( \frac{\partial G}{\partial T_0} \right)_{P_0} + \Delta \left( \frac{\partial G}{\partial P_0} \right)_{T_0} = 0 \quad (37)$$

along the coexistence. Using  $dG$  from Eq. (27) gives us

$$\Delta \left( \frac{\partial G}{\partial T_0} \right)_{P_0} = -\Delta S + (T - T_0) \Delta \left( \frac{\partial S}{\partial T_0} \right)_{P_0} - (P - P_0) \Delta \left( \frac{\partial V}{\partial T_0} \right)_{P_0} - A \Delta \left( \frac{\partial \xi}{\partial T_0} \right)_{P_0} \quad (38)$$

$$\Delta \left( \frac{\partial G}{\partial P_0} \right)_{T_0} = \Delta V + (T - T_0) \Delta \left( \frac{\partial S}{\partial P_0} \right)_{T_0} - (P - P_0) \Delta \left( \frac{\partial V}{\partial P_0} \right)_{T_0} - A \Delta \left( \frac{\partial \xi}{\partial P_0} \right)_{T_0} \quad (39)$$

Putting the above two equations in Eq. (37), we get the following Clausius-Clapeyron equation for coexistence of phases in internal equilibrium

$$\left. \frac{dT_0}{dP_0} \right|_{\text{coex}} = \frac{\Delta V + (T - T_0)\Delta (\partial S/\partial P_0)_{T_0} - (P - P_0)\Delta (\partial V/\partial P_0)_{T_0} - A\Delta (\partial \xi/\partial P_0)_{T_0}}{\Delta S - (T - T_0)\Delta (\partial S/\partial T_0)_{P_0} + (P - P_0)\Delta (\partial V/\partial T_0)_{P_0} + A\Delta (\partial \xi/\partial T_0)_{P_0}}. \quad (40)$$

We now express  $(\partial S/\partial P_0)_{T_0}$  in terms of  $(\partial V/\partial T_0)_{P_0}$  by using the Maxwell relation  $\partial(P, V) = \partial(T, S)$  and by using Eq. (17) ( $F \rightarrow S, K \rightarrow V, x \rightarrow P_0$ , and  $y \rightarrow T_0$ ) as follows:

$$\frac{\partial(S, T_0)}{\partial(P_0, T_0)} = -\frac{\partial(S, T_0)}{\partial(S, T)} \frac{\partial(P, V)}{\partial(P_0, V)} \frac{\partial(P_0, V)}{\partial(P_0, T_0)},$$

which immediately gives

$$\left( \frac{\partial S}{\partial P_0} \right)_{T_0} = -\frac{(\partial P/\partial P_0)_V}{(\partial T/\partial T_0)_S} \left( \frac{\partial V}{\partial T_0} \right)_{P_0}, \quad (41)$$

which can now be used in the Clausius-Clapeyron equation to express it in terms of measurable quantities assuming that  $P, T$  can be measured. In equilibrium,  $T = T_0, P = P_0$  and  $A = 0$ , so that the above equation reduces to the well-known version

$$\left. \frac{dT_0}{dP_0} \right|_{\text{coex}}^{(\text{eq})} = \frac{\Delta V}{\Delta S}, \quad (42)$$

as expected.

## VII. RESPONSE FUNCTIONS IN INTERNAL EQUILIBRIUM

### A. $\bar{C}_P$ and $\bar{C}_V$

The heat capacities with respect to the internal temperature at fixed  $P$  or  $V$  are

$$\begin{aligned} \bar{C}_{P,\xi} &= T \left( \frac{\partial S}{\partial T} \right)_{P,\xi}, & \bar{C}_{V,\xi} &= T \left( \frac{\partial S}{\partial T} \right)_{V,\xi}, \\ \bar{C}_P &= T \left( \frac{\partial S}{\partial T} \right)_P, & \bar{C}_V &= T \left( \frac{\partial S}{\partial T} \right)_V \end{aligned}$$

We again start from the fundamental relation in Eq. (48) and evaluate the derivative

$$T \left( \frac{\partial S}{\partial T} \right)_{P,\xi} = T \left( \frac{\partial S}{\partial T} \right)_{V,\xi} + T \left( \frac{\partial S}{\partial V} \right)_{T,\xi} \left( \frac{\partial V}{\partial T} \right)_{P,\xi},$$

which can be rewritten in two equivalent forms

$$\bar{C}_{P,\xi} = \bar{C}_{V,\xi} + T \left[ \left( \frac{\partial S}{\partial P} \right)_{T,\xi} \left( \frac{\partial V}{\partial T} \right)_{P,\xi} \right] / \left( \frac{\partial V}{\partial P} \right)_{T,\xi} \quad (43)$$

or

$$\bar{C}_{P,\xi} = \bar{C}_{V,\xi} + T \left( \frac{\partial P}{\partial T} \right)_{V,\xi} \left( \frac{\partial V}{\partial T} \right)_{P,\xi}, \quad (44)$$

where we have used the Maxwell relation in Eq. (29) after we divide it by  $\partial(V, T, \xi)$ . As  $(\partial S/\partial P)_{V,\xi}$  is not directly measurable, the identity in Eq. (44) is more useful from a practical point of view. However, we need to transform the various derivatives in it to the derivatives with respect to  $T_0$  at fixed  $P_0$  or  $V$  by using the transformation rules in Sect. III C, as it is the pair  $T_0, P_0$  that can be manipulated by the observer. However, the identities still contains  $\bar{C}_{P,\xi}$  and  $\bar{C}_{V,\xi}$ , which are defined with respect to  $T$ , and not with respect to  $T_0$ . Therefore, we now turn to heat capacities obtained as a derivative with respect to  $T_0$ .

## B. $C_P$ and $C_V$

From Eq. (4), we have

$$C_P \equiv \left( \frac{\partial Q}{\partial T_0} \right)_{P_0} \equiv T \left( \frac{\partial S}{\partial T_0} \right)_{P_0}, \quad C_V \equiv \left( \frac{\partial Q}{\partial T_0} \right)_V \equiv T \left( \frac{\partial S}{\partial T_0} \right)_V, \quad (45)$$

$$C_{P,\xi} \equiv \left( \frac{\partial Q}{\partial T_0} \right)_{P_0,\xi} \equiv T \left( \frac{\partial S}{\partial T_0} \right)_{P_0,\xi}, \quad C_{V,\xi} \equiv \left( \frac{\partial Q}{\partial T_0} \right)_{V,\xi} \equiv T \left( \frac{\partial S}{\partial T_0} \right)_{V,\xi}. \quad (46)$$

It would have been more appropriate to express the capacities  $C_P$  and  $C_{P,\xi}$  as  $C_{P_0}$  and  $C_{P_0,\xi}$ , but we will use the simpler notation. This should cause no confusion. Introducing the expansion coefficient

$$\alpha_P \equiv \frac{1}{V} \left( \frac{\partial V}{\partial T_0} \right)_{P_0}, \quad \alpha_{P,\xi} \equiv \frac{1}{V} \left( \frac{\partial V}{\partial T_0} \right)_{P_0,\xi} \quad (47)$$

we find that

$$\frac{C_P}{\alpha_P} = TV \frac{\partial(S, P_0)/\partial(T_0, P_0)}{\partial(V, P_0)/\partial(T_0, P_0)} = TV \frac{\partial(S, P_0)}{\partial(V, P_0)} = TV \left( \frac{\partial S}{\partial V} \right)_{P_0}.$$

The same discussion can be applied to  $C_{P,\xi}$  and  $\alpha_{P,\xi}$  with a similar result

$$\frac{C_{P,\xi}}{\alpha_{P,\xi}} = TV \frac{\partial(S, P_0, \xi)/\partial(T_0, P_0, \xi)}{\partial(V, P_0, \xi)/\partial(T_0, P_0, \xi)} = TV \frac{\partial(S, P_0, \xi)}{\partial(V, P_0, \xi)} = TV \left( \frac{\partial S}{\partial V} \right)_{P_0,\xi}.$$

Let us now consider the relation between  $C_{P,\xi}$  and  $C_{V,\xi}$  and between  $C_P$  and  $C_V$ , for which we consider  $S$  as a function of  $T, V$  and  $\xi$ , which follows from Eq. (25), so that

$$dS = \frac{\partial S}{\partial T}dT + \frac{\partial S}{\partial V}dV + \frac{\partial S}{\partial \xi}d\xi. \quad (48)$$

Therefore,

$$\left(\frac{\partial S}{\partial T_0}\right)_{P_0,\xi} = \left(\frac{\partial S}{\partial T}\right)_{V,\xi} \left(\frac{\partial T}{\partial T_0}\right)_{P_0,\xi} + \left(\frac{\partial S}{\partial V}\right)_{T,\xi} \left(\frac{\partial V}{\partial T_0}\right)_{P_0,\xi}.$$

Now, using Eq. (18), we have

$$\left(\frac{\partial S}{\partial T}\right)_{V,\xi} = \left(\frac{\partial S}{\partial T_0}\right)_{V,\xi} / \left(\frac{\partial T}{\partial T_0}\right)_{V,\xi} \quad (49)$$

Similarly, using the Maxwell relation in Eq. (30) we have

$$\left(\frac{\partial S}{\partial V}\right)_{T,\xi} = \frac{\partial(V, P, \xi)}{\partial(V, T_0, \xi)} \frac{\partial(V, T_0, \xi)}{\partial(V, T, \xi)} = \left(\frac{\partial P}{\partial T_0}\right)_{V,\xi} / \left(\frac{\partial T}{\partial T_0}\right)_{V,\xi}. \quad (50)$$

We thus finally obtain

$$\left(\frac{\partial S}{\partial T_0}\right)_{P_0,\xi} \left(\frac{\partial T}{\partial T_0}\right)_{V,\xi} = \left(\frac{\partial S}{\partial T_0}\right)_{V,\xi} \left(\frac{\partial T}{\partial T_0}\right)_{P_0,\xi} + \left(\frac{\partial P}{\partial T_0}\right)_{V,\xi} \left(\frac{\partial V}{\partial T_0}\right)_{P_0,\xi},$$

After multiplying by  $T$  on both sides, we obtain the desired relation between  $C_{P,\xi}$  and  $C_{V,\xi}$  for the non-equilibrium case

$$C_{P,\xi} \left(\frac{\partial T}{\partial T_0}\right)_{V,\xi} = C_{V,\xi} \left(\frac{\partial T}{\partial T_0}\right)_{P_0,\xi} + T \left(\frac{\partial P}{\partial T_0}\right)_{V,\xi} \left(\frac{\partial V}{\partial T_0}\right)_{P_0,\xi}. \quad (51)$$

This relation generalize the following standard equilibrium relation:

$$C_P^{\text{eq}} = C_V^{\text{eq}} + T_0 \left(\frac{\partial P_0}{\partial T_0}\right)_V \left(\frac{\partial V}{\partial T_0}\right)_{P_0},$$

obtained by setting

$$\left(\frac{\partial T}{\partial T_0}\right)_{V,\xi} = \left(\frac{\partial T}{\partial T_0}\right)_{P_0,\xi} = 1.$$

We can obtain a standard form of the above heat capacity relations as in Eq. (43) as follows:

$$C_{V,\xi} = T \frac{\partial(S, V, \xi)}{\partial(T_0, V, \xi)} = T \frac{\partial(S, V, \xi)/\partial(T_0, P_0, \xi)}{\partial(T_0, V, \xi)/\partial(T_0, P_0, \xi)}.$$

We thus finally have

$$C_{P,\xi} = C_{V,\xi} + T \frac{(\partial S/\partial P_0)_{T_0,\xi} (\partial V/\partial T_0)_{P_0,\xi}}{(\partial V/\partial P_0)_{T_0,\xi}} = C_{V,\xi} + T \left(\frac{\partial S}{\partial V}\right)_{T_0,\xi} \left(\frac{\partial V}{\partial T_0}\right)_{P_0,\xi}, \quad (52)$$

which is an extension of Eq. (43). Although tedious, it is straightforward to show that this relation is identical to the above relation. One needs to evaluate  $(\partial S/\partial V)_{T_0, \xi}$  as follows:

$$\begin{aligned} \left(\frac{\partial S}{\partial V}\right)_{T_0, \xi} &= \frac{\partial(S, T_0, \xi)}{\partial(V, T, \xi)} \frac{\partial(V, T, \xi)}{\partial(V, T_0, \xi)} \\ &= \left(\frac{\partial T}{\partial T_0}\right)_{V, \xi} \left[ \left(\frac{\partial S}{\partial V}\right)_{T, \xi} \left(\frac{\partial T_0}{\partial T}\right)_{V, \xi} - \left(\frac{\partial S}{\partial T}\right)_{V, \xi} \left(\frac{\partial T_0}{\partial V}\right)_{T, \xi} \right], \end{aligned}$$

where we must now use Eqs. (50) and (49). We finally obtain

$$\left(\frac{\partial S}{\partial V}\right)_{T_0, \xi} = \left(\frac{\partial T}{\partial T_0}\right)_{V, \xi} \left[ \left(\frac{\partial P}{\partial T_0}\right)_{V, \xi} \left(\frac{\partial T_0}{\partial T}\right)_{V, \xi} - \left(\frac{\partial S}{\partial T_0}\right)_{V, \xi} \left(\frac{\partial T_0}{\partial V}\right)_{T, \xi} \right]. \quad (53)$$

The equivalence is now established by the use of the permutation property given in Eq. (11). In a similar fashion, we find that

$$C_P = C_V + T \left(\frac{\partial S}{\partial V}\right)_{T_0} \left(\frac{\partial V}{\partial T_0}\right)_{P_0}, \quad (54)$$

where we must use, see Sect. III B,

$$\left(\frac{\partial S}{\partial V}\right)_{T_0} = \left(\frac{\partial T}{\partial T_0}\right)_V \left[ \left(\frac{\partial P}{\partial T_0}\right)_V \left(\frac{\partial T_0}{\partial T}\right)_V - \left(\frac{\partial S}{\partial T_0}\right)_V \left(\frac{\partial T_0}{\partial V}\right)_T \right] \quad (55)$$

obtained in a similar fashion as Eq. (53).

It is important at this point to relate  $C_P$  with  $C_{P, \xi}$  and  $C_V$  with  $C_{V, \xi}$ . For this, it is convenient to consider the differential  $dS$  by treating  $S$  as a function of  $T_0, P_0$  and  $\xi$ . We find that

$$C_P = C_{P, \xi} + T \left(\frac{\partial S}{\partial \xi}\right)_{T_0, P_0} \left(\frac{\partial \xi}{\partial T_0}\right)_{P_0}, \quad C_V = C_{V, \xi} + T \left(\frac{\partial S}{\partial \xi}\right)_{P_0, V} \left(\frac{\partial \xi}{\partial T_0}\right)_V. \quad (56)$$

### C. Compressibilities $K_T$ and $K_S$

The two important isothermal compressibilities are

$$K_T \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P_0}\right)_{T_0}, \quad K_{T, \xi} \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P_0}\right)_{T_0, \xi},$$

which we need to relate to the corresponding adiabatic compressibility

$$K_S \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P_0}\right)_S, \quad K_{S, \xi} \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P_0}\right)_{S, \xi}.$$

However, we first consider the relation between the compressibility and the expansion coefficient. We find that

$$\frac{K_T}{\alpha_P} = \frac{\partial(V, T_0)/\partial(T_0, P_0)}{\partial(V, P_0)/\partial(T_0, P_0)} = \frac{\partial(V, T_0)}{\partial(V, P_0)} = \left( \frac{\partial T_0}{\partial P_0} \right)_V.$$

The same discussion can be applied to  $K_{T,\xi}$  and  $\alpha_{P,\xi}$  with a similar result

$$\frac{K_{T,\xi}}{\alpha_{P,\xi}} = \left( \frac{\partial T_0}{\partial P_0} \right)_{V,\xi}.$$

The relation between  $K_T$  and  $K_{T,\xi}$  and between  $K_S$  and  $K_{S,\xi}$  are obtained by treating  $V$  as a function of  $T_0, P_0$  and  $\xi$  and of  $S, P_0$  and  $\xi$ , respectively. Using

$$dV = \left( \frac{\partial V}{\partial T_0} \right)_{P_0,\xi} dT_0 + \left( \frac{\partial V}{\partial P_0} \right)_{T_0,\xi} dP_0 + \left( \frac{\partial V}{\partial \xi} \right)_{T_0,P_0} d\xi, \quad (57)$$

$$dV = \left( \frac{\partial V}{\partial S} \right)_{P_0,\xi} dS + \left( \frac{\partial V}{\partial P_0} \right)_{S,\xi} dP_0 + \left( \frac{\partial V}{\partial \xi} \right)_{S,P_0} d\xi, \quad (58)$$

we find that

$$K_T = K_{T,\xi} - \frac{1}{V} \left( \frac{\partial V}{\partial \xi} \right)_{T_0,P_0} \left( \frac{\partial \xi}{\partial P_0} \right)_{T_0}, \quad K_S = K_{S,\xi} - \frac{1}{V} \left( \frac{\partial V}{\partial \xi} \right)_{S,P_0} \left( \frac{\partial \xi}{\partial P_0} \right)_S, \quad (59)$$

which is similar to similar relations for the heat capacity in Eq. (56). We similarly find that

$$\alpha_P = \alpha_{P,\xi} - \frac{1}{V} \left( \frac{\partial V}{\partial \xi} \right)_{T_0,P_0} \left( \frac{\partial \xi}{\partial T_0} \right)_{P_0}. \quad (60)$$

Let us consider  $(\partial V/\partial P_0)_{T_0,\xi}$ :

$$\left( \frac{\partial V}{\partial P_0} \right)_{T_0,\xi} = \frac{\partial(V, T_0, \xi)}{\partial(P_0, T_0, \xi)} = \frac{\partial(V, S, \xi)}{\partial(P_0, S, \xi)} \frac{\partial(P_0, S, \xi)}{\partial(P_0, T_0, \xi)} \frac{\partial(V, T_0, \xi)}{\partial(V, S, \xi)} = \left( \frac{\partial V}{\partial P_0} \right)_{S,\xi} \frac{C_{P,\xi}}{C_{V,\xi}}.$$

Similarly, we find that, see Sect. III B,

$$\left( \frac{\partial V}{\partial P_0} \right)_{T_0} = \left( \frac{\partial V}{\partial P_0} \right)_S \frac{C_P}{C_V}$$

Thus, we have the standard identity for both kinds of compressibility:

$$\frac{C_{P,\xi}}{C_{V,\xi}} \equiv \frac{K_{T,\xi}}{K_{S,\xi}}, \quad \frac{C_P}{C_V} \equiv \frac{K_T}{K_S} \quad (61)$$

Let us again consider  $K_{S,\xi}$ . Rewriting

$$\left( \frac{\partial V}{\partial P_0} \right)_{S,\xi} = \frac{\partial(V, S, \xi)/\partial(P_0, T_0, \xi)}{\partial(P_0, S, \xi)/\partial(P_0, T_0, \xi)} = \left( \frac{\partial V}{\partial P_0} \right)_{T_0,\xi} - \frac{(\partial S/\partial P_0)_{T_0,\xi} (\partial V/\partial T_0)_{P_0,\xi}}{(\partial S/\partial T_0)_{P_0,\xi}},$$

we find that

$$K_{T,\xi} \equiv K_{S,\xi} - \frac{(\partial S/\partial P_0)_{T_0,\xi} (\partial V/\partial T_0)_{P_0,\xi}}{V(\partial S/\partial T_0)_{P_0,\xi}} = K_{S,\xi} - (\partial S/\partial P_0)_{T_0,\xi} (\partial V/\partial S)_{P_0,\xi}..$$

### VIII. PRIGOGINE-DEFAY RATIO

Let us consider Figs. 2 and 3 again that describe various kinds of glass transitions: the apparent transitions at  $T_{0G}$  (point D) and  $T_{0g}^{(A)}$  (point C) and the conventional transitions at  $T_{0G}$  (point D) and  $T_{0g}$  (point B). From the discussion in Sect. II, we know that the Gibbs free energies have a discontinuity between the two states involved at the apparent transitions. Even the volumes and the entropies exhibit discontinuities at these transitions. On the other hand, the Gibbs free energies, volumes and entropies have no discontinuities at the conventional transitions at  $T_{0G}$  and  $T_{0g}$  due to the continuity of the state. Let us introduce the difference

$$\Delta q \equiv q_I - q_{II} \quad (62)$$

for any quantity  $q$  at a given  $T_0, P_0$  in the two possible states I and II. For the apparent glass transition at  $T_{0G}$ ,  $q_I, q_{II}$  are the values of  $q$  in GL and L, respectively, at  $T_{0G}$ ; for the apparent glass transition at  $T_{0g}^{(A)}$ ,  $q_I, q_{II}$  are the values of  $q$  in gL and L, respectively at  $T_{0g}^{(A)}$ . For the conventional glass transition at  $T_{0G}$ ,  $q_I, q_{II}$  are the values of  $q$  in the glass GL and gL, respectively, at  $T_{0G}$ ; for the precursory glass transition at  $T_{0g}$ ,  $q_I, q_{II}$  are the values of  $q$  in gL and L, respectively at  $T_{0g}$ . These states are summarized in the Table below.

Table: Various States

	Apparent $T_{0G}$	Apparent $T_{0g}^{(A)}$	Conventional $T_{0g}$	Conventional $T_{0G}$
I	GL	gL	gL	GL
II	L	L	L	gL

In terms of the discontinuities  $\Delta C_P, \Delta K_T$  and  $\Delta \alpha_P$ , the Prigogine-Defay ratio [9] is traditionally defined as [9–13, 23–25]

$$\Pi^{\text{trad}} \equiv \frac{\Delta C_P \Delta K_T}{V T_0 (\Delta \alpha_P)^2},$$

where it is assumed that the volume is the same in both states at  $T_0, P_0$ , as is evident from earlier work. As we will see below, the volume is normally not continuous at the apparent glass transitions, used in most experimental and theoretical analyses of the glass transition. To allow for this possibility, we will consider the following equivalent definition

of the Prigogine-Defay ration in this work:

$$\Pi \equiv \frac{\Delta C_P \Delta K_T}{T_0(\Delta V \alpha_P)(\Delta \alpha_P)}, \quad (63)$$

where we have absorbed  $V$  in one of the  $\Delta \alpha_P$ -factors. It is clear that  $\Pi$  is not different from  $\Pi^{\text{trad}}$  when the volume is the same as happens for conventional transitions.

As the experimentalists have no control over the internal variables, and can only manipulate the observables  $\mathbf{X}$  by controlling the fields  $\mathbf{y}_0$  of the medium, we will discuss the evaluation of the Prigogine-Defay ratio in the subspace of  $\mathbf{y}_0$  of the complete thermodynamic space of  $\mathbf{y}_0, \mathbf{a}_0$ . We will consider the simplest possible case in which the subspace reduces to the  $T_0$ - $P_0$  plane. Therefore, we will restrict ourselves to this plane in the following, knowing very well that the GL and gL are also determined by the set  $\xi$  of internal variables; see Sect. III B. We will consider the general case of several internal variables  $\xi_k, k = 1, 2, \dots, n$ .

### A. Conventional Transitions at $T_{0g}$ and $T_{0G}$

We will first consider the Prigogine-Defay ratio  $\Pi_g$  at the conventional transitions at points B and D (see Figs. 2 and 3). The continuity of the state across B and D means that  $E, V$  and  $S$  remain continuous across the conventional transitions at B and D. This is consistent with the continuity of the Gibbs free energy. Let us first consider the transition at B, where the relaxation time  $\tau$  of the system becomes equal to the observation time-scale  $\tau_{\text{obs}}$ , so that both states gL and L remain in equilibrium with the medium. Thus,  $T = T_0, P = P_0$ , and  $\mathbf{A} = \mathbf{A}_0 = 0$  for both states at B. Therefore, there is no need to consider the internal variables in the Gibbs free energy, as they are not independent variables. Moreover,  $V = (\partial G / \partial P_0)_{T_0}$  and  $S = -(\partial G / \partial T_0)_{P_0}$ . Thus, the Gibbs free energy and its derivatives with respect to  $T_0, P_0$  are continuous at B; the second derivatives need not be. It is clear that B represents a point that resembles a continuous transition in equilibrium; it turns into a glass transition curve  $T_{0g}(P_0)$  of continuous transitions in the  $T_0$ - $P_0$  plane.

For the transition at D, we have a glass GL on the low-temperature side, and gL at the high temperature side; both states are out of equilibrium and have the same temperature  $T(t)$  and pressure  $P(t)$ , different from  $T_0, P_0$ , respectively at the transition. Similarly,  $A(t) \neq 0$  is the same in both states. The important characteristics of the conventional transitions are the continuity of  $E, V$  and  $S$  at B and D. We now follow the consequences of these

continuities.

### 1. Continuity of Volume

From the continuity of the volume, we have

$$d\Delta_g \ln V = \Delta_g \left( \frac{\partial \ln V}{\partial T_0} \right)_{P_0} dT_0 + \Delta_g \left( \frac{\partial \ln V}{\partial P_0} \right)_{T_0} dP_0 = 0, \quad (64)$$

where  $\Delta_g q$  denotes the difference in Eq. (62) at the conventional glass transitions, and the derivatives are also evaluated at the transition points. This equation can be written in terms of the compressibilities and the expansion coefficients in the two states at the glass transition temperature  $T_{0g}$  or  $T_{0G}$ :

$$\left. \frac{dT_0}{dP_0} \right|_{tr} = \frac{\Delta_g K_T}{\Delta_g \alpha_P}; \quad (65)$$

the isothermal compressibility  $K_T$  and the isobaric expansion coefficient  $\alpha_P$  are given in Eqs. (45) and (47), respectively, and can be expressed in terms of the derivatives of the internal variable  $\xi$ , such as given in Eqs. (59) and (60) for a single internal variable  $\xi$ . We make no assumption about these  $\xi$ -derivatives, such as their vanishing or any assumption about freezing of  $\xi$  at its value at B; indeed, we expect  $\xi$  to change continuously over BC. Of course, we must remember that  $\xi$  is an independent thermodynamic variable in gL and GL states only, and not in the L state [2]. The slope equation (65) determines the variation of  $T_{0g}$  or  $T_{0G}$  with the medium pressure  $P_0$  along the glass transition curve  $T_{0g,G}(P_0)$  in the  $T_0$ - $P_0$  plane, regardless of  $\xi$ . The form of the above equation does not depend on the number of internal variables, provided we use the proper definitions of  $K_T$  and  $\alpha_P$  as given in Eqs. (45) and (47), respectively. Its form follows from the continuity of the volume at the conventional glass transition.

### 2. Continuity of Entropy

From the continuity of the entropy at  $T_{0g}$ , we similarly have

$$d\Delta_g S = \Delta_g \left( \frac{\partial S}{\partial T_0} \right)_{P_0} dT_0 + \Delta_g \left( \frac{\partial S}{\partial P_0} \right)_{T_{0g}} dP_0 = 0, \quad (66)$$

from which we obtain at the precursory glass transition at B

$$\left. \frac{dT_{0g}}{dP_0} \right|_{tr} = \frac{T_0 \Delta_g (V \alpha_P)}{\Delta_g C_P} = \frac{V_g T_0 \Delta_g \alpha_P}{\Delta_g C_P}, \quad (67)$$

where we have used the equilibrium Maxwell relation  $(\partial S/\partial P_0)_{T_0} = -(\partial V/\partial T_0)_{P_0} = V\alpha_P$ ; see Eq. (7) or Eq. (41) applied to this case. Here  $V_g$  is the common volume of gL and L at B and has been taken out of  $\Delta_g(V\alpha_P)$ . Again, this relation for the slope is quite general, independent of the number of internal variables in gL state at lower temperatures  $T_0 < T_{0g}$ . Accordingly,

$$\Pi_g \equiv \frac{\Delta_g C_P \Delta_g K_T}{V_g T_0 (\Delta_g \alpha_P)^2} = 1, \quad (68)$$

as expected for equilibrium states. It is a consequence of the glass transition being a continuous transition between equilibrium states at B. As we will see below, it is not merely a consequence of the continuity of volume and entropy simultaneously.

Let us now consider the glass transition at  $T_{0G}$ . It follows from Eq. (45) that

$$\Delta_g \left( \frac{\partial S}{\partial T_0} \right)_{P_0} = \frac{\Delta_g C_P}{T}.$$

In conjunction with Eq. (41), we find that

$$\frac{dT_{0G}}{dP_0} \Big|_{tr} = \frac{V_G T \Delta_g \alpha_P}{\Delta_g C_P} \frac{(\partial P/\partial P_0)_V}{(\partial T/\partial T_0)_S},$$

where  $V_G$  is the common volume of gL and GL at D and has been taken out of  $\Delta_g(V\alpha_P)$ .

We finally obtain

$$\Pi_G \equiv \frac{\Delta_g C_P \Delta_g K_T}{V_G T_0 (\Delta_g \alpha_P)^2} = \frac{T}{T_0} \frac{(\partial P/\partial P_0)_V}{(\partial T/\partial T_0)_S} \neq 1 \quad (69)$$

for the conventional glass transition at D. The deviation of  $\Pi_G$  from unity is independent of the number of internal variables. It will be different from unity even if we have no internal variables.

## B. Apparent Glass Transitions at $T_{0g}^{(A)}$ and $T_{0G}$

Unfortunately, it is not a common practice to determine the Prigogine-Defay ratio at the conventional transitions at temperatures  $T_{0g}(P_0)$  or  $T_{0G}(P_0)$ , which resemble continuous transition in that the volume and entropy are continuous, along with the Gibbs free energy. In experiments, one determines the ratio at apparent glass transitions either at D or at  $T_{0g}^{(A)}(P_0)$  in the glass transition region BD; see Figs. 2 and 3. In these transitions, there are discontinuities in the  $G, E, V$  and  $S$ . The extrapolated point C (see Fig. 2) identifies the apparent glass transition temperature  $T_{0g}^{(A)}(P_0)$ , which cannot be treated as a transition

temperature because the Gibbs free energy in the two states (gL and L) are not equal, as is clearly seen in Fig. 3. It is clear from Fig. 2 that the volume is also different in gL and L at the apparent glass transition  $T_{0g}^{(A)}(P_0)$ . The discontinuity of the volume should not be confused with the continuity of the *extrapolated* volumes used to determine the location of the phenomenological glass transition  $T_{0g}^{(A)}(P_0)$ . The extrapolated glass volume does not represent the physical volume of the glass at  $T_{0g}^{(A)}(P_0)$  given by the point on the curve BD in Fig. 2. The discontinuity is between the physical volumes of gL and L at  $T_{0g}^{(A)}(P_0)$ . We already know that both the entropy and the enthalpy of the glass continue to decrease during vitrification as the system relaxes [1]. Indeed, the volume of the glass or gL also relaxes towards that of the supercooled liquid L. This will also be true at  $T_{0g}^{(A)}(P_0)$  so that the volume and the entropy of gL are higher than their values in the supercooled liquid at  $T_{0g}^{(A)}(P_0)$  in a vitrification process. The same sort of discontinuities also occur at D. In the following, we will take into account these discontinuities in the volume and entropy in determining the Prigogine-Defay ratio at the apparent glass transitions at  $T_{0G}(P_0)$  and  $T_{0g}^{(A)}(P_0)$ . The discontinuity of volume  $\Delta_g^{(A)}V \neq 0$  causes a modification of Eq. (64) at these transitions:

$$\left. \frac{dT_0}{dP_0} \right|_{\text{tr}} = \frac{\delta \ln V_P^{(A)} + \Delta_g^{(A)} K_T}{\Delta_g^{(A)} \alpha_P} = \frac{\Delta_g^{(A)} K_T}{\Delta_g^{(A)} \alpha_P} (1 + \delta_g^{(A)} V_P) \quad (70)$$

in terms of

$$\delta \ln V_P^{(A)} \equiv d\Delta_g^{(A)} \ln V / dP_0 \Big|_{\text{tr}} \quad (71)$$

at  $T_{0g}^{(A)}$  or  $T_{0G}$ , as the case may be; the three  $\Delta_g^{(A)}$ 's are the difference  $\Delta$  in Eq. (62) evaluated at  $T_{0g}^{(A)}$  or  $T_{0G}$ , and the new quantity  $\delta_g^{(A)} V_P$  has an obvious definition:

$$\delta_g^{(A)} V_P = \frac{\delta \ln V_P^{(A)}}{\Delta_g^{(A)} K_T} \quad (72)$$

at the appropriate temperature. This contribution would vanish under the approximation  $\Delta_g^{(A)} \ln V \simeq 0$ , or  $\delta \ln V_P^{(A)} \simeq 0$ . The slope equation (70) must always be satisfied at the apparent glass transition temperature. The quantity  $\delta \ln V_P^{(A)}$  in it represents the variation of the discontinuity

$$\Delta_g^{(A)} \ln V = \ln V_I(T_0, P_0) - \ln V_{II}(T_0, P_0)$$

with pressure along the apparent glass transition curve  $T_{0g}^{(A)}(P_0)$  or  $T_{0G}(P_0)$ , and can also be found experimentally. Indeed, we can treat  $\Delta_g^{(A)} \ln V$  as a function of  $P_{0g} \equiv P_0(T_{0g}^{(A)})$  along

the transition curves. Then the contribution from the volume discontinuity is given by

$$\delta \ln V_P^{(A)} = \frac{1}{V_I} \left. \frac{dV_I(P_0)}{dP_0} \right|_{\text{tr}} - \frac{1}{V_{II}} \left. \frac{dV_{II}(P_0)}{dP_0} \right|_{\text{tr}}. \quad (73)$$

We can use Eqs. (59) and (60) to express the slope in terms of  $\Delta_g K_{T,\xi}$  and  $\Delta_g \alpha_{P,\xi}$ :

$$\left. \frac{dT_0}{dP_0} \right|_{\text{tr}} = \frac{\delta \ln V_P^{(A)} + \Delta_g^{(A)} K_{T,\xi} - V_{\xi,I} \partial \xi / \partial P_0|_{\text{tr}} / V_I}{\Delta_g^{(A)} \alpha_{P,\xi} - V_{\xi,I} \partial \xi / \partial T_0|_{\text{tr}} / V_I}, \quad (74)$$

where  $V_{\xi,G}$  represents the derivative  $(\partial V_I / \partial \xi)_{T_0, P_0}$ , and  $V_I$  is the GL volume at  $T_{0G}$  or the gL volume at  $T_{0g}^{(A)}$ . The  $\xi$ -contribution from the L state is absent due to the vanishing of the affinity  $\mathbf{A}_0 (= 0)$  in the L.

Let us now consider the differential of the entropy difference at the apparent glass transition in the  $T_0$  -  $P_0$  plane:

$$d\Delta_g^{(A)} S = \Delta_g^{(A)} \left( \frac{\partial S}{\partial T_0} \right)_{P_0} dT_0 + \Delta_g^{(A)} \left( \frac{\partial S}{\partial P_0} \right)_{T_0} dP_0,$$

from which we find that

$$\left. \frac{dT_0}{dP_0} \right|_{\text{tr}} = \frac{\delta S_P^{(A)} - \Delta_g^{(A)} (\partial S / \partial P_0)_{T_0}}{\Delta_g^{(A)} (\partial S / \partial T_0)_{P_0}}, \quad (75)$$

with

$$\delta S_P^{(A)} \equiv d\Delta_g^{(A)} S / dP_0|_{\text{tr}}; \quad (76)$$

it represents the rate of variation of the entropy discontinuity

$$\Delta_g^{(A)} S = S_I(T_0, P_0) - S_{II}(T_0, P_0)$$

along the apparent glass transition curves. Following the steps in deriving Eq. (73), we find that the contribution from the entropy discontinuity is given by

$$\delta S_P^{(A)} = \left. \frac{dS_I(P_0)}{dP_0} \right|_{\text{tr}} - \left. \frac{dS_{II}(P_0)}{dP_0} \right|_{\text{tr}}. \quad (77)$$

The derivative  $(\partial S_I / \partial P_0)_{T_0}$  in the second term in the numerator in Eq. (75) can be manipulated as in Eq. (41):

$$\frac{\partial(S, T_0)}{\partial(P_0, T_0)} = - \frac{\partial(S, T_0)}{\partial(V, P_0)} \frac{\partial(P_0, V)}{\partial(P_0, T_0)} = - \left( \frac{\partial V}{\partial T_0} \right)_{P_0} \frac{\partial(S, T_0)}{\partial(V, P_0)},$$

in which the last Jacobian reduces to unity under equilibrium by the use of the Maxwell relation  $\partial(V, P = P_0) = \partial(S, T = T_0)$ . We, therefore, write

$$\frac{\partial(S, T_0)}{\partial(V, P_0)} = \frac{(\partial P / \partial P_0)_V}{(\partial T / \partial T_0)_S} = 1 + \delta S_{VS}^I$$

for the glassy state; this equation also defines the modification  $\delta S_{VP}^I$  given by

$$\delta S_{VS}^I = \frac{(\partial P / \partial P_0)_V}{(\partial T / \partial T_0)_S} - 1 \quad (78)$$

for the glassy state, where  $T, P$  are the internal temperature, pressure of the glassy state. It vanishes under the approximation  $T = T_0$  and  $P = P_0$ . We now have

$$\left( \frac{\partial S_I}{\partial P_0} \right)_{T_0} = - \left( \frac{\partial V_I}{\partial T_0} \right)_{P_0} (1 + \delta S_{VS}^I) = -V_I(1 + \delta S_{VS}^I)\alpha_P^I.$$

For the supercooled liquid, which represents an equilibrium state, we evidently have ( $S_{II} \equiv S_L$ )

$$\left( \frac{\partial S_L}{\partial P_0} \right)_{T_0} = - \left( \frac{\partial V_L}{\partial T_0} \right)_{P_0} = -V_L\alpha_P^L,$$

so that

$$\Delta_g^{(A)} (\partial S / \partial P_0)_{T_0} = -\Delta_g^{(A)}(V\alpha_P) - V_I\alpha_P^I\delta S_{VS}^I.$$

We now turn to the denominator in Eq. (75). For the supercooled liquid state, whose temperature is  $T_0$ , we have

$$\left( \frac{\partial S_L}{\partial T_0} \right)_{P_0} = \frac{C_P^L}{T_0};$$

we must use  $T_{0g}^{(A)}$  or  $T_{0G}$  for  $T_0$  to evaluate this slope at the appropriate apparent glass transition. For the glass, whose internal temperature is  $T$ , we have

$$\left( \frac{\partial S_I}{\partial T_0} \right)_{P_0} = \frac{C_P^I}{T} \equiv (1 + \delta T^I) \frac{C_P^I}{T_0},$$

where we have introduced a correction parameter

$$\delta T^I \equiv T_{0g,G}^{(A)}/T - 1, \quad (79)$$

with  $T_{0g,G}^{(A)}$  denoting  $T_{0g}^{(A)}$  or  $T_{0G}$  as the case may be. Again, this modification term vanishes under the approximation  $T = T_0$ . We thus find that

$$T_0 \Delta_g^{(A)} (\partial S / \partial T_0)_{P_0} = \Delta_g^{(A)} C_P + C_P^I \delta T^I.$$

Equating the two different versions of the slope in Eqs. (70) and (75), we have

$$\begin{aligned} \frac{\Delta_g^{(A)} K_T}{\Delta_g^{(A)} \alpha_P} (1 + \delta_g^{(A)} V_P) &= T_{0g,G}^{(A)} \frac{\delta S_P^{(A)} + \Delta_g^{(A)} (V \alpha_P) + V_I \alpha_P^I \delta S_{VS}^I}{\Delta_g^{(A)} C_P + C_P^I \delta T^G} \\ &\equiv \frac{T_{0g,G}^{(A)} \Delta_g^{(A)} (V \alpha_P)}{\Delta_g^{(A)} C_P} (1 + \delta' \Pi_{gA}), \end{aligned}$$

where we have introduced a new quantity  $\delta' \Pi_{gA}$ , whose definition is obvious from the equality.

We finally find that the Prigogine-Defay ratio is given by

$$\Pi_{gA} \equiv \frac{\Delta_g^{(A)} C_P \Delta_g^{(A)} K_T}{T_{0g,G}^{(A)} \Delta_g^{(A)} \alpha_P \Delta_g^{(A)} (V \alpha_P)} \equiv 1 + \delta \Pi_{gA} \equiv \frac{1 + \delta' \Pi_{gA}}{1 + \delta_g^{(A)} V_P} \quad (80)$$

at the apparent glass transition. Its complete form is given by

$$\Pi_{gA} = \frac{1 + \left( V_I \alpha_P^I \delta S_{VS}^I + \delta S_P^{(A)} \right) / \Delta_g^{(A)} (V \alpha_P)}{(1 + C_P^I \delta T^I / \Delta_g^{(A)} C_P) (1 + \delta_g^{(A)} V_P)}. \quad (81)$$

It should be obvious that the Prigogine-Defay ratio is itself a function of time as it depends on time-dependent quantities such as  $\Delta_g^{(A)} S$ ,  $\delta T^I$ , etc.

### 1. Approximation A

Let us assume that the discontinuities in the volume and entropy are negligible or that the contributions  $\delta \ln V_P^{(A)}$  and  $\delta S_P^{(A)}$  are negligible. In that case, the Prigogine-Defay ratio reduces to

$$\Pi_{gA} \simeq \frac{1 + V_I \alpha_P^I \delta S_{VS}^I / \Delta_g^{(A)} (V \alpha_P)}{1 + C_P^I \delta T^I / \Delta_g^{(A)} C_P},$$

and will have a value different than 1. Thus, the continuity of volume and entropy alone is not sufficient to yield  $\Pi_{gA} = 1$ , as noted above. If we further approximate  $T \simeq T_0$  and  $P \simeq P_0$ , then  $\delta S_{VS}^I \simeq 0$  and  $\delta T^I \simeq 0$ , and we obtain  $\Pi_{gA} \simeq 1$ . This is expected as the approximations change the apparent glass transition into a continuous transition. If, however, we only assume  $P \simeq P_0$ , but allow  $T$  to be different from  $T_0$ , then

$$\delta S_{VS}^I \simeq \frac{1}{(\partial T / \partial T_0)_{S_I}} - 1,$$

and we still have  $\Pi_{gA} \neq 1$ .

## 2. Approximation B

We make no assumption about  $\delta \ln V_P^{(A)}$  and  $\delta S_P^{(A)}$ , but approximate  $T \simeq T_0$  and  $P \simeq P_0$ .

In this case,  $\delta S_{VS}^I \simeq 0$  and  $\delta T^I \simeq 0$ , and we obtain

$$\Pi_{gA} \simeq \frac{1 + \delta S_P^{(A)} / \Delta_g^{(A)}(V\alpha_P)}{1 + \delta_g^{(A)} V_P}.$$

If, however, the approximation  $T \simeq T_0$  is not valid, we have

$$\Pi_{gA} \simeq \frac{1 + \delta S_P^{(A)} / \Delta_g^{(A)}(V\alpha_P)}{(1 + C_P^I \delta T^G / \Delta_g^{(A)} C_P)(1 + \delta_g^{(A)} V_P)}.$$

In both cases,  $\Pi_{gA} \neq 1$ .

## C. Comparison with Other Attempts for $\Pi$

As far as we know, almost all previous attempts [9–13, 23–25] in the evaluation of  $\Pi$  are based on treating the glass transition as a *direct* transition from L to GL; the structure is supposed to be almost frozen in the latter. As we see from Figs. 2 and 3, this can only occur at C between L and the extrapolated branch DC. At C, there will be a discontinuity between the values of the internal variable  $\xi$ ; it will take the equilibrium value  $\xi_C^{eq}$  in L, but will take a non-equilibrium value  $\xi_C^{extra} \neq \xi_C^{eq}$  obtained along DC. Similarly,  $A = A_0 = 0$  in L at C, while  $A = A_C \neq 0$  in the extrapolated GL at C. As C is obtained by matching the volumes, the volume remains continuous, but there is no reason to believe that the entropy will remain continuous in this transition. The Gibbs free energy obviously remains discontinuous in this transition.

However, we have been careful in not treating this transition as an apparent transition above for the simple reason that there is no guarantee that the branch DC can be described by vitrification thermodynamics at the constant cooling rate  $r$ . To see it most easily, we observe that as the cooling rate is gradually taken to be slower and slower, the transition point B gradually moves towards C along BF. However, the analog of BD will most certainly not be identical to DC for the simple reason that the state of L will continuously change to gL so that the values of  $\xi$  and  $A$  in gL at C will be identical to their values  $\xi = \xi_C^{eq}$  and  $A = 0$  in L at C. Moreover, there is no guarantee that the extrapolated branch DC can even satisfy thermodynamics with known controllable parameters  $T_0, P_0$  and  $r$ . To treat this “transition” as a glass transition requires some approximation, which we have avoided.

## IX. CONCLUSIONS

We have followed the consequences of internal equilibrium to derive generalizations of equilibrium thermodynamic relations such as Maxwell's relations, Clausius-Clapeyron relation, relations between response functions (heat capacities, compressibilities, etc.) to non-equilibrium systems. Non-equilibrium states are described not only by internal fields (temperature, pressure, etc.) that are different from the medium, but also described by internal variables which cannot be controlled from outside by the observer. The observer can only control the observables. Thus, in this work, we have also discussed how the thermodynamics should be described in the subspace of the observables only. As glasses are a prime example of non-equilibrium states, we have reviewed the notion of the glass transition. The frozen structure known as the glass (GL) does not emerge directly out of the equilibrium supercooled liquid (L). There is an intermediate non-equilibrium state (gL) that is not yet frozen when it emerges continuously out of the equilibrium liquid L. At a lower temperature, this state continuously turns into GL. Because of this, we find that there is no one unique non-equilibrium transition. We introduce four of the most conceptually useful transitions. At two of them, which we term conventional glass transitions, the Gibbs free energies and the states are continuous. Thus, they are the non-equilibrium analog of the conventional continuous or second order transition between equilibrium states. At the other two glass transitions, which we term apparent glass transition, not only the states but also the Gibbs free energies are discontinuous. Because of this, these transitions are examples of a zeroth order transition where the free energy is discontinuous. But there is no transition in the system itself at the apparent glass transition as discussed in Sect. II.

We briefly review the use of Jacobians which are found extremely useful in obtaining the generalization of the Maxwell relations. There are many other Maxwell relations than reported here; they can be easily constructed. We then discuss various response functions and obtain relationship between them in non-equilibriums states. Surprisingly, many of these relations look similar in form to those found in equilibrium thermodynamics.

We finally evaluate the Prigogine-Defay ratio at the four possible glass transitions. We find that the ratio is normally different than 1, except at the conventional glass transition at the highest temperature, where it is always equal to 1, regardless of the number of internal variables. We also find that the continuity of volume and entropy is not a guarantee for

$\Pi = 1$ . We compare our analysis of  $\Pi$  with those carried out by other workers.

**Acknowledgement 1** *P.P. Aung was supported by a summer internship from NSF through the University of Akron REU site for Polymer Science.*

## Appendix A: Relation between 2- and 3-Jacobians

Let us consider a function  $F(x, y, z)$ , where  $x, y, z$  may stand for  $T_0, P_0, \xi$ , respectively.

Then

$$dF = F_{x,yz}dx + F_{y,zx}dy + F_{z,xy}dz,$$

where we have used the compact notation

$$F_{x,yz} \equiv \left( \frac{\partial F}{\partial x} \right)_{yz},$$

etc. Now,

$$\left( \frac{\partial F}{\partial x} \right)_y = F_{x,yz} + F_{z,xy} \left( \frac{\partial z}{\partial x} \right)_y.$$

Similarly,

$$\left( \frac{\partial K}{\partial y} \right)_x = K_{y,zx} + K_{z,xy} \left( \frac{\partial z}{\partial y} \right)_x.$$

We express  $F_{x,yz}$  as a 3-Jacobian and manipulate it as follows:

$$\begin{aligned} \frac{\partial(F, y, z)}{\partial(x, y, z)} &= \frac{\partial(F, y, z)}{\partial(K, x, z)} \frac{\partial(K, x, z)}{\partial(x, y, z)} = \frac{\partial(F, y, z)}{\partial(K, x, z)} \left[ - \left( \frac{\partial K}{\partial y} \right)_x + K_{z,xy} \left( \frac{\partial z}{\partial y} \right)_x \right] \\ &= - \left( \frac{\partial K}{\partial y} \right)_x \left[ \frac{\partial(F, y, z)}{\partial(K, x, z)} - K_{z,xy} \left( \frac{\partial z}{\partial K} \right)_x \frac{\partial(F, y, z)}{\partial(K, x, z)} \right]. \end{aligned}$$

Using this, we find that

$$\left( \frac{\partial F}{\partial x} \right)_y = - \left( \frac{\partial K}{\partial y} \right)_x \left[ \frac{\partial(F, y, z)}{\partial(K, x, z)} - K_{z,xy} \left( \frac{\partial z}{\partial K} \right)_x \frac{\partial(F, y, z)}{\partial(K, x, z)} + F_{z,xy} \frac{\partial(z, y)}{\partial(K, x)} \right].$$

Let us call the quantity in the square brackets  $D$ , which can be rewritten as

$$D \equiv \frac{\partial(F, y)}{\partial(K, x)} D',$$

where

$$D' = \frac{\partial(F, y, z)}{\partial(K, x, z)} \frac{\partial(K, x)}{\partial(F, y)} - K_{z,xy} \frac{\partial(z, x)}{\partial(F, y)} \frac{\partial(F, y, z)}{\partial(K, x, z)} + F_{z,xy} \frac{\partial(z, y)}{\partial(F, y)}.$$

Using Eq. (14), it can now be shown in a straight-forward manner that

$$D' = 1,$$

which proves that

$$\left( \frac{\partial F}{\partial x} \right)_y = - \left( \frac{\partial K}{\partial y} \right)_x \frac{\partial(F, y)}{\partial(K, x)},$$

the desired result.

While we considered  $F$  and  $K$  as a function of 3 variables, we can generalize the result to any number of variables. We will not pause here to do that.

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